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LOCKHEED MARTIN



**ENVIRONMENTAL
RESTORATION
PROGRAM**

**Final Project Report on Arsenic
Biogeochemistry in the Clinch River
and Watts Bar Reservoir**

Volume 1: Main Text

MANAGED BY
LOCKHEED MARTIN ENERGY SYSTEMS, INC.
FOR THE UNITED STATES
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ENERGY SYSTEMS



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Energy Systems Environmental Restoration Program
Clinch River Environmental Restoration Program

**Final Project Report on Arsenic Biogeochemistry
in the Clinch River and Watts Bar Reservoir**

Volume 1: Main Text

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ABBREVIATIONS

ATSDR	Agency for Toxic Substances and Disease Registry
BRSP	Bull Run Steam Plan
COD	chemical oxygen demand
CR/WBR	Clinch River/Watts Bar Reservoir
CR-ERP	Clinch River Environmental Restoration Program
CRK	Clinch River kilometer
DO	dissolved oxygen
DOE	U.S. Department of Energy
Energy Systems	Martin Marietta Energy Systems
EPA	U.S. Environmental Protection Agency
ESD	Environmental Sciences Division
HDPE	high-density polyethylene
HGAAS	hydride generation atomic absorption spectrophotometry
IC	ion chromatography
ICP	inductively coupled plasma
KSP	Kingston Steam Plant
LCS	laboratory control sample
LMBE	lower McCoy Branch Embayment
LWBR	lower Watts Bar Reservoir
MCBK	McCoy Branch kilometer
NAWQC	National Ambient Water Quality Criteria
NPDES	National Pollutant Discharge Elimination System
ORNL	Oak Ridge National Laboratory
ORR	Oak Ridge Reservation
PCK	Poplar Creek kilometer
QA/QC	quality assurance/quality control
QC	quality control
RI/FS	remedial investigation/feasibility study
RPD	relative percent difference
RQ	Rogers Quarry
SAS	Statistical Analysis Systems
SOP	standard operating procedures
TRK	Tennessee River kilometer
TVA	Tennessee Valley Authority
UMBE	upper McCoy Branch Embayment

PREFACE

This study was conducted as a special project of the Clinch River Remedial Investigation, which is tasked with conducting a remedial investigation of the Clinch River and Watts Bar Reservoir by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA). The Clinch River Environmental Restoration Program is funded by the U. S. Department of Energy to investigate the possible corrective actions required to rectify the historic releases of hazardous waste and radioactive contaminants into the Clinch River/Watts Bar Reservoir system. The arsenic study was undertaken after preliminary screening of existing data from the Clinch River and Watts Bar Reservoir. As a result of nonconservative screening, arsenic was assigned as a definitely high priority substance for further human health consideration, and the data showed that arsenic concentrations exceeded benchmark criteria for ecological risk assessment. This study investigated the speciation, distribution, and mobility of arsenic in the sediment, pore water, and the water column seasonally over a 3-year period (1990-1992).



EXECUTIVE SUMMARY

This document reports on the study of arsenic contamination in the Clinch River/Watts Bar Reservoir (CR/WBR) system, downstream from the U.S. Department of Energy's Oak Ridge Reservation (ORR). Arsenic is of particular interest and concern because (1) it occurs commonly in coal-bearing rock and waste products, such as fly ash associated with the burning of coal; (2) it is classified as a Class A carcinogen by the Environmental Protection Agency; and (3) disposal of fly ash, both on and off the ORR, may have contaminated surface water and sediments in the Clinch River and Watts Bar Reservoir.

The present study differs from previous reports on arsenic concentrations in the CR/WBR system because investigators used much more sensitive and precise processing and analytical techniques to measure arsenic species (arsenate, arsenite, and organic arsenic) at levels well below the ecological and human health risk screening criteria. Absolute detection limits with these techniques are approximately 20 to 40 pmol/L, or 0.0015 to 0.003 $\mu\text{g/L}$. The human health cancer risk value corresponding to a 10^{-4} risk is 4.7 $\mu\text{g/L}$ (62 nM). Arsenic concentrations greater than or equal to 11 $\mu\text{g/L}$ (146 nM) exceed the hazard index for human health toxicity. Ecological risk values are based on the National Ambient Water Quality Criteria for Protection of Aquatic Life, which is intended to protect most aquatic species from excess exposure. Values of 190 $\mu\text{g/L}$ (2536 nM) for arsenite [As(III)] and 8.1 $\mu\text{g/L}$ (108 nM) for arsenate [As(V)] exceeded lower ecological screening benchmarks (*Toxicological Benchmarks for Screening Potential Contaminants of Concern for Effects on Aquatic Biota*, 1994, G. W. Suter II and J. B. Mabry, ES/ER/TM-96/R1, Oak Ridge National Laboratory).

Four main sites were sampled quarterly over a 3-year period (1990 through 1992). Sites investigated included lower Watts Bar Reservoir (LWBR) near Watts Bar Dam [Tennessee River kilometer (TRK) 849.6], the Kingston area [Clinch River kilometer (CRK) 1.6], Poplar Creek [Poplar Creek kilometer (PCK) 1.6], and the McCoy Branch Embayment [McCoy Branch kilometer (MBK) 0.3]. Additional sites were investigated in the vicinity of these main stations to determine the distribution of contamination and to identify possible alternative or additional sources of arsenic.

Seasonal increases in dissolved inorganic arsenic in bottom waters in LWBR were attributable to fluxes of dissolved arsenic from sediments during conditions of low dissolved oxygen. The maximum arsenic concentration under low dissolved oxygen conditions was 8.9 nM (0.67 $\mu\text{g/L}$). Surface water arsenic concentrations did not exceed the minimum ecological risk screening concentrations.

Inorganic arsenic levels were elevated in surface waters (0 to 5 m deep) in the Kingston area. Values dropped with depth in the water column and were at their lowest near the sediment-water interface. Surface water arsenic contamination in this area did not appear to originate on the ORR. An arsenic source to the surface water in the Kingston area is suspected.

In Poplar Creek, sediments found deeper than 15 cm were grossly contaminated with arsenic. Sediment pore water values averaged 38,000 nM (2,850 $\mu\text{g/L}$). Surface sediment

arsenic concentrations were not different from those observed at Kingston, LWBR, or in Melton Hill Reservoir, upstream. The Poplar Creek site historically received fly ash directly from disposal operations at the K-25 Site on the ORR until 1963. Evidence suggests that deposition and accumulation of cleaner sediment since 1963, in combination with stream-like water flow rates and oxic conditions throughout the water column, may be preventing significant sedimentary release of arsenic to the surface waters in Poplar Creek.

Arsenic concentrations in Rogers Quarry outfall (MBK 1.6) dropped greatly during this study as a result of actions taken to curtail and eventually eliminate fly ash disposal in Rogers Quarry. However, arsenic concentrations in the Rogers Quarry discharge were in excess of both human health and ecological risk screening criteria for all sample collection periods. Arsenic concentrations in surface waters (0 to 2 m deep) decreased with distance downstream in McCoy Branch. Maximum summer values in upper McCoy Branch Embayment (MBK 0.85 and MBK 0.7) exceeded human health risk screening criteria. Winter concentrations were significantly lower. The maximum summer values in lower McCoy Branch Embayment (MBK 0.5 and MBK 0.3) were elevated, but were significantly lower than upper McCoy Branch Embayment and significantly higher than at CRK 60.5, approximately 0.25 km downstream in Melton Hill Reservoir.

Seasonal increases in dissolved inorganic arsenic were observed both in the sediment pore waters and surface waters throughout the McCoy Branch Embayment downstream from Rogers Quarry. Seasonal change was not observed either upstream (MBK 2) or downstream (MBK 1.6) from Rogers Quarry. Changes in surface water arsenic values in McCoy Branch Embayment may be attributed largely to seasonal changes in sediment pore water chemistry, rather than to changes in Rogers Quarry outflows.

Based on observed concentration differences within the surface sediments and between the surface sediment and overlying surface water, the apparent flux of arsenic from sediment pore waters was greatest by far in upper McCoy Branch Embayment, followed by lower McCoy Branch Embayment, Poplar Creek, and LWBR. Concentrations in excess of risk screening values were observed only in upper McCoy Branch Embayment. The degree to which sediments serve as a source of dissolved arsenic on a seasonal basis should be evaluated more thoroughly by performing arsenic flux calculations at these sites.

The elevated surface water arsenic concentrations in the Kingston area (CRK 8 to TRK 907.2, approximately 8 km) were much more extensive than for McCoy Branch Embayment (MBK 0.85 to the McCoy Branch mouth, approximately 0.85 kilometers). The aerial extent of surface water contamination in the Kingston area is approximately 10 times greater than for McCoy Branch Embayment. If a more extensive investigation were conducted in the Kingston area, it is likely that arsenic concentrations similar to those observed in Rogers Quarry surface waters would also be found for the Kingston contamination source.

Detection limits that were a factor of 20 below the minimum risk screening criteria were achieved for 100% of arsenic speciation data. However, 118 samples for inductively coupled plasma metals analysis were not preserved to analytical specifications, and the analytical holding times for 180 ion chromatography samples were not met. More rigorous preservative testing protocols and more tightly defined analytical statements of work will prevent these problems in the future.

Introduction, background, materials and methods, results, discussion, and conclusions are presented in Volume 1. The Quality Assurance/Quality Control Summary Report; the listing of water quality and surface water arsenic speciation data by source and site; and the listing of pore water arsenic speciation and particle-to-water distribution coefficients for arsenic, iron, and manganese by source, site, and season are presented in Volume 2.

The Clinch River Environmental Restoration Program is currently completing its second phase of the Clinch River Remedial Investigation, with the intent of performing a baseline risk assessment on the collected data. The data collected for this report will contribute to the baseline risk assessment. Many of the goals of the Clinch River Remedial Investigation were refined using the results of this study.

1. INTRODUCTION

1.1 PURPOSE

This study was initiated to investigate arsenic contamination in the Clinch River/Watts Bar Reservoir (CR/WBR) environment, downstream from the U.S. Department of Energy (DOE) Oak Ridge Reservation (ORR). Specifically, this study investigated the speciation, distribution, and mobility of arsenic in the sediment, pore water, and the water column seasonally over a 3-year period (1990-1992). The study was conducted as a special project of the Clinch River Environmental Restoration Program (CR-ERP), by personnel affiliated with the Environmental Sciences Division of the Oak Ridge National Laboratory (ORNL), and it was funded by DOE. The CR-ERP was initiated to investigate the possible corrective actions required to rectify the historic releases of hazardous waste and radioactive contaminants into the CR/WBR system. The arsenic study was undertaken following preliminary screening of existing data from the Clinch River and Watts Bar Reservoir, which assigned arsenic as a definitely high priority substance for further human health consideration, as a result of nonconservative screening (Hoffman et al. 1991, Table 4.1), and showed that arsenic concentrations exceeded benchmark criteria for ecological risk assessment (Suter 1991, Table 2). These same reports specified that more sensitive detection methods be used to more adequately quantify the arsenic concentrations in CR/WBR surface waters. Because arsenic is classified as toxic and carcinogenic [Agency for Toxic Substances and Disease Registry (ATSDR) 1989], it is considered a high priority substance for further investigation in the CR/WBR system (Hoffman et al. 1991, Cook et al. 1992).

Arsenic occurs naturally in surface waters as a result of rock and soil weathering or geothermal activity. Anthropogenic sources for arsenic contamination include mining and smelting waste, combustion of fossil fuels, and use of pesticides and herbicides (ATSDR 1989). Disposal of fly ash from coal-fired steam plants is an important source of arsenic contamination in CR/WBR sediments. As illustrated in Fig. 1, the predominant form of arsenic in the CR/WBR system is moderately insoluble in oxic water; therefore, sediments are the primary repository for arsenic. Reducing (anoxic) conditions in sediments may cause the release of dissolved arsenic from sediment solids to the interstitial water between the sediment solids (pore water); dissolved arsenic then may be conveyed from the pore water into the water column. This dissolution may occur in the water column under anoxic conditions (Fig.1).

The predominant chemical forms of arsenic in natural waters are arsenate [As(V)] and arsenite [As(III)]. The toxicity, carcinogenicity, and physiological behavior of arsenic depend on the predominant chemical form (see Chap. 2); in this report, inorganic arsenic is the sum of As(III) and As(V). The human health cancer risk value (1 in 10,000 risk of incidence of excess cancer using a 30-year occupational exposure period that includes a 40-h work week, 50 weeks per year) is 62 nM (4.7 µg/L) for inorganic arsenic. Arsenic concentrations greater than or equal to 146 nM (11 µg/L) exceed the hazard index for human health toxicity [Environmental Protection Agency (EPA) 1989, Hoffman et al. 1991]. The arsenic concentration for human health toxicity is not for a specific species. Few of the historical studies on which this limit is based measured the chemical species of arsenic. Since most

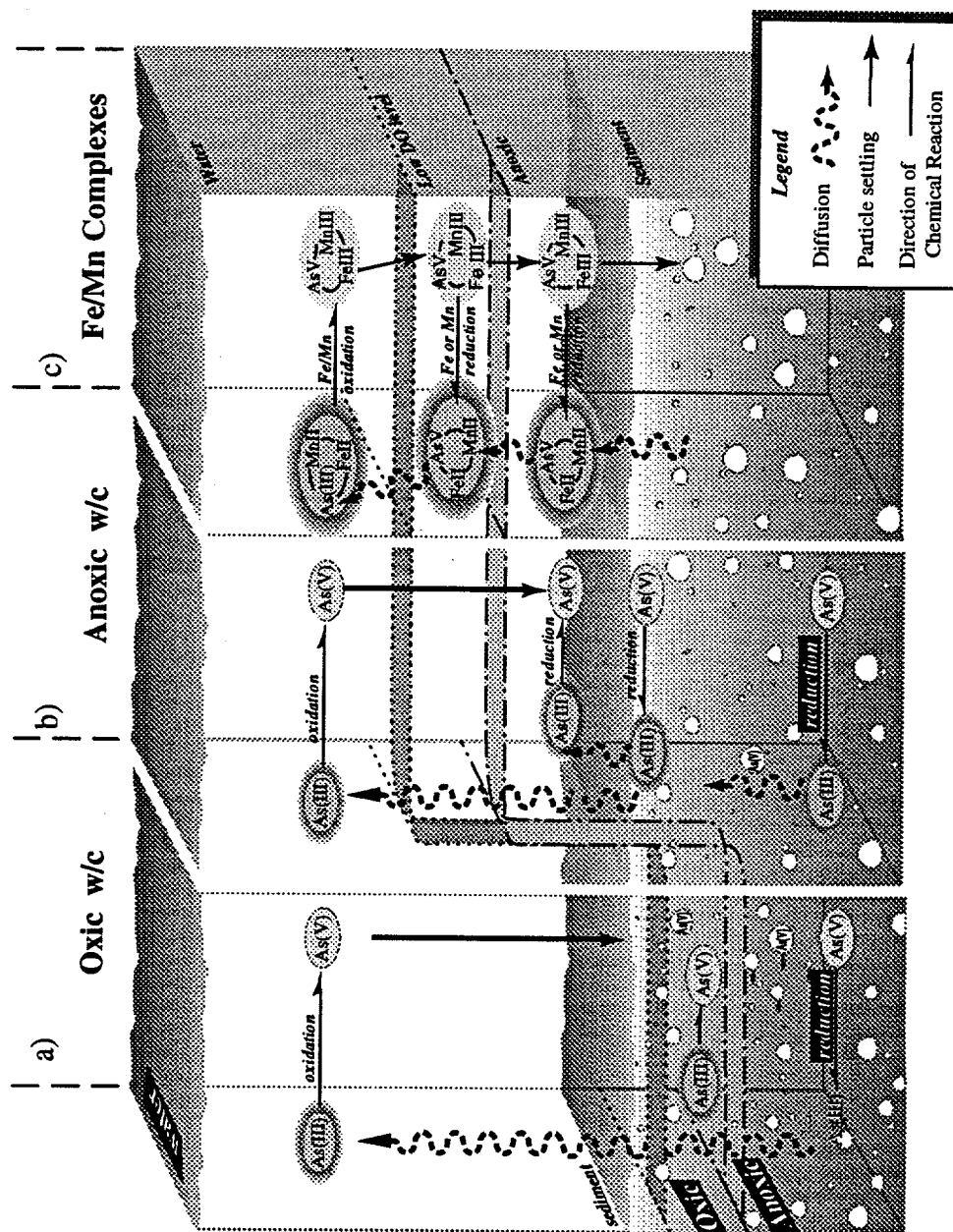


Fig. 1. Conceptual diagram of arsenic dynamics between sediments and surface water in a freshwater ecosystem: (a) fully oxidizing water column, (b) partially reduced water column, (c) iron and manganese complexes in a partially reduced water column.

potential human exposure is through ingestion of treated surface water, a presumption may be made that the oxidized form, As(V), is most prevalent; however, recent studies indicate that in groundwater exposure scenarios, the reduced form, As(III), predominates. Ecological risk analysis, based upon the National Ambient Water Quality Criteria (NAWQC) for Protection of Aquatic Life, is intended to protect most aquatic species. Values of 190 $\mu\text{g/L}$ (2536 nM) for As(III) and 8.11 $\mu\text{g/L}$ (108 nM) for As(V) exceed lower screening benchmarks (Suter and Mabry 1994). A previous benchmark chronic value for As(V) was deemed excessively conservative and has been replaced by the Tier II secondary chronic value (Suter and Mabry 1994, Table 1). Ecological risk benchmark values account for all possible exposure routes involving environments containing both predominately arsenite and predominately arsenate.

Data on the concentration of arsenic in surface waters and sediments both on the ORR (Kornegay et al. 1992) and elsewhere in the CR/WBR system (TVA 1991) have been reported with either values or detection limits that were greater than the risk screening criteria; detection limits for total arsenic in these reports ranged from 13 to 2670 nM (1 to 200 $\mu\text{g/L}$), depending on the analytical methodology used. Additionally, standard analytical techniques do not yield values for the different chemical forms of arsenic. By using more sensitive techniques, the present study measured total inorganic arsenic, arsenite, arsenate, and organic arsenic at concentrations well below these risk criteria, with detection limits between 0.02 and 0.04 nM (0.0015 and 0.003 $\mu\text{g/L}$).

1.2 SCOPE

Arsenic distribution was investigated at four main sites in the CR/WBR system, as illustrated in Fig. 2 and summarized in Table 1. Additional surface water and sediment samples were collected in the proximity of known and suspected sources to the CR/WBR system to more completely characterize arsenic distributions. Results from sites with few sample collection events and no observed influences on arsenic distribution are not presented.

1.3 OBJECTIVES

The primary objectives of this study are to (1) assess arsenic speciation, distribution, and mobility in sediment, sediment pore water, and the water column; (2) evaluate the mobilization of contaminants from deposited sediments; (3) determine the soluble and insoluble concentration of inorganic As, reduced As [As(III)], oxidized As [As(V)], methyl As species, the concentrations of other metals and major cations, and surface water quality parameters of sites in the surface water, sediment pore water, and sediments representative of the full range of possible arsenic contamination in the CR/WBR system; (4) investigate temporal and spatial changes in arsenic concentrations from representative sites in the CR/WBR system; (5) determine seasonal changes in sediment-water distribution coefficients (K_D) for arsenic and metals that are known to be significantly related to arsenic movement between sediments and surface waters, and (6) focus future investigations on any areas observed to significantly affect arsenic distribution in the CR/WBR system.

The data quality required to meet these objectives includes (1) obtaining very low analytical detection limits to routinely detect arsenic in the CR/WBR system, below the human health and ecological risk limit values; (2) maintaining geochemical conditions

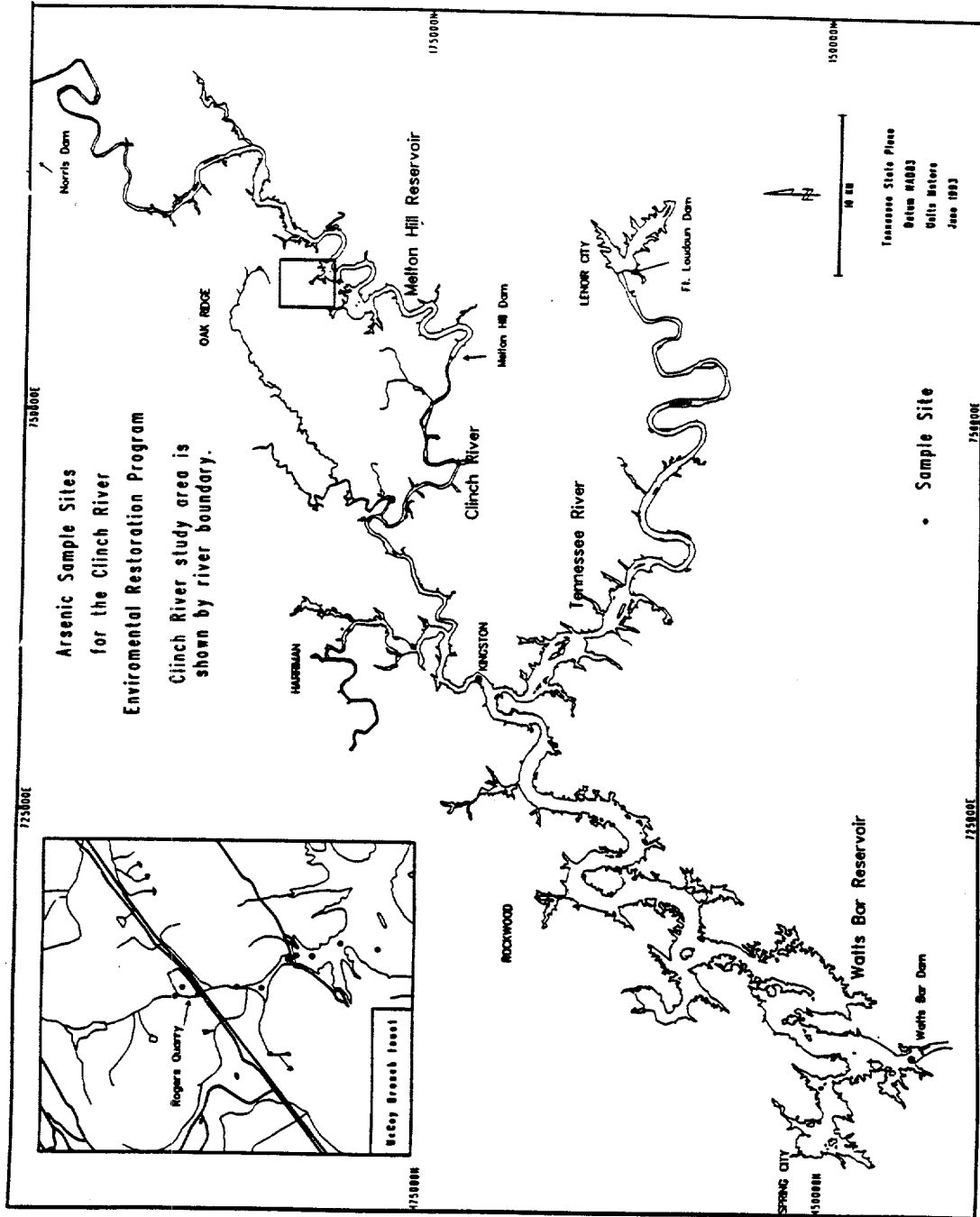


Fig. 2. Location of the four main sites that were investigated for arsenic distribution in this study.

in sediment pore water samples from the time of collection to preservation and analysis; (3) measuring analyte concentrations in very small volume pore water samples, necessitated by centrifugation of small sediment sections to remove pore water; and (4) determining arsenic concentrations in surface waters and sediment pore waters above background values.

Table 1. Matrix of dates and sites sampled for the arsenic biogeochemistry study of the CR/WBR system

Site (river kilometer)	March 1990 (spring)	July 1990 (summer)	August 1990 (summer)	January 1991 (winter)	March 1991 (spring)	July 1991 (summer)	February 1992 (winter)	June, July 1992 (summer)	October 1992 (fall)	December 1992 (winter)
Lower Watts Bar Source										
TRK 849.6 ^a	19 ^b /0 ^c	12/0	10/17	17/0	8/11	10/11	9/11	10/11	10/10	0/0
Kingston Source										
TRK 907.2	6/0	6/0	0/0	6/0	0/0	0/0	0/0	0/0	0/0	0/0
CRK 1.6	6/0	5/0	6/12	5/0	4/9	5/11	5/8	5/11	5/9	0/0
CRK 4	1/0	1/0	0/0	1/0	0/0	0/0	0/0	0/0	0/0	0/0
CRK 5.6	1/0	1/0	0/0	1/0	0/0	0/0	0/0	0/0	0/0	0/0
CRK 8	6/0	5/0	0/0	5/0	0/0	0/0	0/0	0/0	0/0	0/0
Poplar Creek Source										
PCK 1.6 ^d	0/0	0/0	8/13	5/0	3/8	6/15	4/13	4/12	4/11	0/0
Lower McCoy Branch Embayment Source										
CRK 60.5	4/0	6/0	0/0	1/0	0/0	0/0	0/0	5/8	0/0	5/8
McBK 0.3 ^e	5/0	6/0	0/0	7/0	7/8	7/10	7/11	5/10	5/12	5/11
McBK 0.5 ^f	0/0	1/0	0/0	1/0	1/0	1/0	1/0	3/5	0/0	3/5
Upper McCoy Branch Embayment Source										
McBK 0.7 ^g	0/0	1/0	0/0	1/0	1/0	1/0	1/0	4/11	0/0	4/11
McBK 0.85 ^h	0/0	0/0	0/0	1/0	1/0	1/0	0/0	2/10	0/0	1/8

Table 1 (continued)

Site (river kilometer)	March 1990 (spring)	July 1990 (summer)	August 1990 (summer)	January 1991 (winter)	March 1991 (spring)	July 1991 (summer)	February 1992 (winter)	June, July 1992 (summer)	October 1992 (fall)	December 1992 (winter)
Rogers Quarry Source										
McBK 1.6 ⁱ	3/0	1/0	0/0	1/0	1/0	2/0	j	j	j	j
McBK 1.8	0/0	0/0	0/0	0/0	0/0	0/0		3/0		
McBK 2	1/0	1/0	0/0	1/0	1/0	1/0				
Upper Melton Hill Reservoir Source										
CRK 66.7	1/0	1/0	0/0	1/0	0/0	0/0	0/0	0/0	0/0	0/0
CRK 73.6	1/0	6/0	0/0	0/0	0/0	0/0	0/0	0/0	0/0	0/0
CRK 78.4	0/0	1/0	0/0	0/0	0/0	0/0	0/0	0/0	0/0	0/0
CRK 80	1/0	1/0	0/0	1/0	0/0	0/0	0/0	0/0	0/0	0/0

ⁱIncludes surface water samples from TRK 863.2 in March 1990 (5), July 1990 (7), and January 1991 (8), and TRK 875.2 in March 1990 (5).

^jNumber of water samples collected per sampling event.

^kNumber of sediment sections collected per sampling event. See text for details on length of sediment cores.

^lIncludes one surface water sample each (0.0-m) from CRK 18.4, PCK 0.25, and CRK 20 in August 1990.

^mIncludes surface water and sediment samples from McBK 0.35 in June 1992 (3/7).

ⁿIncludes surface water samples (0.0 m) from McBK 0.56 in July 1990, January 1991, March 1991, July 1991, and February 1992; also includes surface water and sediment samples from McBK 0.4 in June 1992 (4/10) and December 1992 (4/8).

^oIncludes surface water samples (0.0 m) from McBK 0.66 in July 1990, January 1991, March 1991, July 1991, and February 1992.

^pIncludes surface water samples (0.0 m) from McBK 0.9 in March 1991 and July 1991.

^qIncludes surface water samples (0.0 m) from McBK 1.0 in March 1990 and McBK 1.2 in March 1990 and July 1991.

^rSee Volume 2 listing of weekly sample collection data from McBK 2, McBK 1.8, and McBK 1.6 for Rogers Quarry, February 1992 through March 1993.

2. BACKGROUND

River-reservoir systems serve as efficient repositories for suspended particles and contaminants associated with these particles (Thornton et al 1990, Olsen et al 1992). Additionally, stream embayments off of the main stem, river-reservoir systems may serve as the primary repositories for suspended sediments and sediment associated contaminants (Blaylock et al 1993, Cook et al. 1992).

Arsenic toxicity is strongly influenced by both its physical (soluble or insoluble) and chemical (oxidized or reduced) forms (ATSDR 1989). Dissolved total inorganic arsenic, either As(V) or As(III), is more mobile and appears to be more toxic than insoluble total inorganic arsenic (ATSDR 1989). Arsenite, [As(III)], the thermodynamically stable form under low oxygen environments, is less strongly adsorbed to particles and more toxic than arsenate, [As(V)] (Masscheleyn et al. 1991).

The role of Fe and Mn in the mobility and cycling of arsenic in sedimentary environments has been well established (Aggett and O'Brien 1985, Takamatsu et al 1985, Peterson and Carpenter 1986, Brannon and Patrick 1987, Belzile and Tessier 1990, Mok and Wai 1990). Though insoluble in its thermodynamically stable form [at neutral pH and moderate dissolved oxygen (DO) levels], As(V) may also be associated with Fe or Mn and become soluble at moderate DO levels (Edenborn et al. 1986, Masscheleyn et al. 1991). At high DO, As(V) associates with insoluble ferric and manganate oxyhydroxides. Manganese undergoes oxidation and reduction reactions more readily than Fe or As, becoming reduced and soluble at high oxygen levels relative to those for Fe or As. With the reduction and subsequent solution of these Mn and Fe compounds when exposed to low DO levels, often resulting from burial within the sediment column, As(V) may then be released to the pore water (Aggett and Kriegman 1988, Brannon and Patrick 1987). As DO levels drop, first the Mn, then ferric iron, and finally As(V) ions are reduced and solubilized, primarily by anaerobically respiring bacteria (Masscheleyn et al. 1991, Fig. 1; Edenborn et al. 1986, Table 2); these elements are used as substitutes for oxygen in anaerobic respiration, and are converted to soluble forms. The rates of reduction are slow in the absence of anaerobic bacteria (Aggett and Kriegman 1988). Dissolved inorganic arsenic is very mobile and may migrate within the sediments or across the sediment-water interface into the water column (Kuhn and Sigg 1993, Sealer and Martin 1989). The cycle is complete when arsenic is then deposited back to the sediments in environments with elevated DO levels, where either Fe and Mn form insoluble oxyhydroxides or As(III) is oxidized to As(V), as illustrated in Fig. 1(a and b). It is expected then that inorganic arsenic levels will increase in the water column near the sediment-water interface, or any source of arsenic due to decreasing DO levels resulting from anaerobic reduction of Mn and Fe, formation of soluble associations in the sediments, and releases from the sediments to the overlying water.

The relative amount of arsenic diffusing to the water column from the sediments and its physical state depend on (1) the pH and DO content of the water, which controls the rate of Fe and Mn oxidation, and (2) the position of the boundary between oxidizing and reducing environments, also known as the redox boundary. If the water column is depleted of oxygen and the redox boundary exists in the lower water column, the flux of a specific constituent from the sediments to the water column will be determined solely by the difference in concentration between sediment and water (the concentration gradient), the molecular diffusion coefficient, bioturbation, and other physical mixing processes. The redox boundary

is compound-specific, as discussed earlier for As, Fe, and Mn. If the water column is well oxygenated and the redox boundary exists in the sediment, most of the dissolved arsenic will be scavenged onto sediment particles from the pore waters before reaching the sediment-water interface. The depth at which the redox boundary is found may change over the course of a year, alternately dissolving arsenic from the solids and re-associating arsenic with solids.

Given the sensitivity of As, Fe, and Mn to changes in environmental parameters, the particle-to-water distribution coefficient (K_D) may change dramatically over the course of a season. The K_D is calculated by dividing the concentration in the solid phase (e.g., nanomoles per kilogram dry sediment) by that in the corresponding liquid phase (e.g., nanomoles per liter of pore water) to yield values in terms of liters of dissolved constituent per kilogram of solid constituent as follows:

$$K_D = (\text{nanomoles As/kg dry sediment}) / (\text{nanomoles As/L pore water})$$

For As, Fe, and Mn, changes in K_D with depth and over time in sediments at the same site, and also with depth and over time between sites, serves as a tool for determining the relative importance of particular metals to the release of arsenic and other inorganic contaminants (Edenborn et al. 1986, Brannon and Patrick, 1987). Highly particle reactive substances, such as cesium, have K_D values in the range of 2×10^5 to 5×10^5 , while dissolved substances such as calcium have K_D values of less than 100. For this study, arsenic K_D values ranged between 10 and 2×10^4 .

Throughout this report, the units of Molarity (moles per liter) are used. This terminology is preferred by biogeochemists because it facilitates comparisons made between different chemical species of the same element or between elements. This capability is particularly necessary for comparisons of co-precipitation, oxidation/reduction reactions, or calculation of a chemical charge balance between major ions. The conversion between Molarity and mass based concentrations ($\mu\text{g/L}$ or ppm) is as follows:

$$1 \text{ micromole As/L} = 74.92135 \mu\text{g As/L}$$

All dissolved values in the report are in nanomolar (nM) where $1 \text{ nM As} = 0.7491235 \mu\text{g As/L}$. Molar values for sediment solids for calculation of arsenic K_D values are derived by conversion from dry sediment concentrations, using calculated sediment porosity. See Sect. 3.3.2 for details.

3. MATERIALS AND METHODS

3.1 SITE DESCRIPTION

Four sites were sampled quarterly over the 3-year period: Watts Bar Dam, Tennessee River kilometer (TRK) 849.6; Kingston City Park, Clinch River kilometer (CRK) 1.6; Poplar Creek, Poplar Creek kilometer (PCK) 1.6; and McCoy Branch Embayment, McCoy Branch kilometer (MCBK) 0.3. The Poplar Creek and McCoy Branch Embayment sites are within the boundaries of the ORR, although both are in public waters (Fig. 2).

The lower Watts Bar Reservoir (LWBR) site [Tennessee River kilometer (TRK) 849.6] with a 26.5-m maximum water depth is located 3 km above Watts Bar Dam (TRK 846.4) and 58 km below the confluence of the Clinch and Tennessee rivers. Watts Bar Dam is the first impoundment of the Tennessee River downstream of the ORR. Contaminants released from upstream sources in the Watts Bar watershed should accumulate in LWBR sediments. The water column in LWBR is deep enough that a reduced oxygen environment may exist during summer stratification, influencing the chemistry of arsenic and other compounds. This site was sampled for surface water arsenic content on nine occasions and for sediment pore water arsenic content on six occasions, at least once each season (Table 1). Additional surface water samples were collected within LWBR (from TRK 863 and TRK 875.2) to measure spatial trends. The differences in water chemistry and arsenic among these sites were small compared to the changes seen at other sites. No further sampling was conducted at these additional sites.

The Kingston site [Clinch River kilometer (CRK) 1.6], with a 12-m maximum water depth, is above the confluence of the Clinch and Tennessee rivers. The site is of particular interest because (1) it is 2 km downstream from the Tennessee Valley Authority's (TVA's) coal-fired Kingston Steam Plant (KSP), (2) it is 2 km from the drinking water intake for the city of Kingston, and (3) it is the location of the first major sediment deposition zone downstream of the ORR (Olsen et al. 1992). Although this site is relatively shallow, the possibility exists for thermal stratification of the water column; water flow rates in this area tend to be greater than observed in lower Watts Bar. The Kingston site was sampled for surface water arsenic content on nine different occasions and for pore water arsenic content on six occasions. Additional sampling was conducted to better define the arsenic source to the surface waters in the Kingston area. Sampling consisted of surface water grab samples from CRK 4 and CRK 5.6 and water column profiles from TRK 907.2, downstream from the Clinch River mouth, and CRK 8, upstream from the Emory River mouth.

Poplar Creek, the largest stream draining the ORR, has its confluence with the Clinch River at CRK 19. The Poplar Creek site (PCK 1.6), with a 5-m maximum water depth, is in the vicinity of a fly ash disposal area in Poplar Creek; this site has the potential for elevated arsenic levels in the sediment and surface water. Fly ash was disposed of directly into Poplar Creek from 1953 until 1963 (Ashwood et al. 1986). The PCK 1.6 site was sampled for surface water arsenic content on seven occasions and for sediment pore waters on six occasions. This sampling occurred at least once each season (Table 1). As with the lower Watts Bar and Kingston sites, additional surface water samples were collected to determine spatial trends in surface water arsenic. These sites include downstream at CRK 18.4, near the Poplar Creek mouth at PCK 0.25, and upstream at CRK 20 (Table 1).

The McCoy Branch Embayment, located on the ORR, is an impoundment of the Clinch River formed by Melton Hill Dam (located at CRK 37). McCoy Branch receives drainage from coal fly ash disposal sites on Chestnut Ridge before flowing through Rogers Quarry (RQ) prior to its confluence with the Clinch River at CRK 60.5 (Ryon 1992). Coal ash was also disposed of to varying degrees directly in RQ until 1992. The McCoy Branch area encompasses lower McCoy Branch Embayment (LMBE) (CRK 60.5, MCBK 0.3, MCBK 0.35, MCBK 0.4, MCBK 0.5 and MCBK 0.56), upper McCoy Branch Embayment (UMBE) (MCBK 0.66, MCBK 0.7, MCBK 0.85 and MCBK 0.9), and the RQ outfall (MCBK 1, MCBK 1.2, MCBK 1.4, MCBK 1.6 and MCBK 1.8). Differences in water chemistry, surface water and pore water arsenic between MCBK 0.3 and MCBK 0.35 were small relative to changes observed between other sites; data from these sites are combined as MCBK 0.3. Differences in water chemistry, surface water, and pore water arsenic between MCBK 0.4, MCBK 0.5 and MCBK 0.56 were small relative to changes observed between other sites; data from these sites are combined as MCBK 0.5. Differences in water chemistry, surface water, and pore water arsenic between MCBK 0.66 and MCBK 0.7 were small relative to changes observed between other sites; data from these sites are combined as MCBK 0.7. Differences in water chemistry, surface water, and pore water arsenic between MCBK 0.85 and MCBK 0.9 were small relative to changes observed between other sites; data from these sites are combined as MCBK 0.85. Differences in water chemistry, surface water, and pore water arsenic between MCBK 1.0, MCBK 1.2, MCBK 1.4 and MCBK 1.6 were small relative to changes observed between other sites; data from these sites are combined as MCBK 1.6. MCBK 2 is included in the RQ outfall, though it is upstream from RQ. Sample collection seasons and dates are summarized in Table 1. The outfall at MCBK 1.6 was modified in March 1992 to enhance the discharge of deep water (greater than 10 m) from RQ. From February 1992 through April 1993, surface water grab samples for arsenic determination were collected weekly from the inflow (MCBK 2), surface (MCBK 1.8), and outflow (MCBK 1.6) areas of RQ. Weekly sample collection was designed to coincide with weekly National Pollutant Discharge Elimination System (NPDES) monitoring at the RQ outfall (NPDES Permit # TN0002968, outfall 302). Weekly monitoring results include pH, chemical oxygen demand (COD), turbidity and arsenic were reported with weekly arsenic values.

Surface water in the Bull Run Steam Plant (BRSP) area, a TVA coal-fired electrical generating plant, were collected to evaluate whether the BRSP contributed significant quantities of arsenic to the surface waters of Melton Hill Reservoir. Surface water samples were collected from Melton Hill Reservoir at the Oak Ridge Marina (CRK 80), immediately upstream from the BRSP (CRK 78.4), at the BRSP outfall (CRK 73.6), and at the drinking water intake for the City of Oak Ridge (CRK 66.7). Sample collection dates are summarized in Table 1.

3.2 FIELD SAMPLING

Water column physical/chemical conditions were measured using pre-calibrated Hydrolab Surveyor multi-parameter water quality monitoring devices, following the CR-ERP Standard Operating Procedures (Energy Systems 1995) for measurement of surface water physical/chemical parameters (Energy Systems 1995). Water quality measured includes water temperature (degrees C, range 5 to 30°C), pH (range 7.5 to 8.5 units) and DO (% saturation, range 0 to >100%); DO was recorded as milligrams per liter in the field and converted to percent saturation using the equation for oxygen solubility at a given temperature and correcting for depth (Standard Methods 1985). Temperature values vary greatly with season

and depth in the water. Though pH can vary a great deal with season and depth in the water column, primarily as a result of photosynthesis or respiration, the narrow range of pH measurements suggests that it has a limited influence on the oxidizing or reducing nature of the CR/WBR water column during this study. DO values also vary with season and depth in the water column. Low DO values (<60% saturation) are evidence of an increasingly reducing environment caused by microbial respiration or other strictly chemical process that requires oxygen to proceed; high values (>90%) indicate an increasingly oxidizing environment. The impact of pH or DO changes on chemical species is discussed in Chap. 2.

Water column samples were collected from multiple depths representative of the water column, using a pre-cleaned (i.e., Milli-Q water rinse) PVC Van Dorn style sampler, following standard operating procedures (Energy Systems 1995). Field samples were placed in pre-cleaned (i.e., acid bath, Milli-Q water rinse) 0.5 L and 4.0 L polyethylene containers. Samples were chilled in ice chests and returned to the processing laboratory within 2 h of collection.

Sediment cores were collected using a free-fall Wildco® KB gravity corer, equipped with precleaned (i.e., a Milli-Q water rinse) polycarbonate liners (120 cm long, 4.7 cm diameter), following standard CR-ERP procedures (Energy Systems 1995). Sediment cores were collected after the water quality data and water sample collection were completed. Upon collection, sediment core tubes were placed in an upright position and protected from direct sunlight until processed.

3.3 ESD LABORATORY PROCESSING

3.3.1 Water Analysis

One set of water samples for inorganic determinations were filtered through 0.45- μ m syringe filters (Whatman Puradisc) that had been washed with acid and rinsed with Milli-Q water. After filtering, the samples were split into two aliquots. The first aliquot was placed in a precleaned beaker and titrated with standardized ultrapure 0.1 N HCl (Ultrapure) for alkalinity determination following the *Gran* procedure (Stumm and Morgan 1970). Alkalinity data for water samples near the sediment-water interface and in the pore water are reported in milliequivalents per liter (meq/L). Values may be converted to milligrams per liter by multiplying by a factor of 50; alkalinity results are found in Volume 2. After acidification from the alkalinity determination, this sample was submitted to an inductively coupled plasma (ICP) scan for analysis of metal constituents (Sect. 3.4). Additional acid to ensure that pH < 2 was not added because of concerns about dilution of the sample by preservative. The second aliquot (chilled) was submitted for analysis of major ion content by ion chromatography (IC) (Sect. 3.4).

A second set of two aliquots was pressure filtered through acid-washed, 0.45- μ m Millipore filters for arsenic speciation determinations. Of these two, the first aliquot was placed in precleaned 0.125-L high-density polyethylene (HDPE) bottles and frozen until analyzed for As(III) (Sect. 3.5). The final aliquot was placed in precleaned 0.25-L HDPE bottles and acidified to pH 2 with 6 M HCl (4 mL HCl/L of sample) and submitted for total inorganic arsenic analysis (Sect. 3.5). Arsenate [As(V)] was determined by difference between the total inorganic arsenic and As(III) results.

3.3.2 Sediment Analysis

The top portion of each sediment core was sectioned into 3-cm increments, followed by 6-cm increments for the rest of the core. Each section was placed in a pre-tared (Mettler PJ3600 balance), precleaned (i.e., Milli-Q rinsed and air-flow bench dried) 0.25-L HDPE bottle, prefilled with argon gas and capped. Argon gas minimizes changes in sediment chemistry due to exposure to the air. Each section was weighed and then centrifuged using a Beckman centrifuge at 5500 rpm for 20 min. Sediment sections yielded between 20 and 50 mL of pore water, a quantity minimally sufficient for standard analytical determinations, though adequate for the methods used during this study. Centrifuged bottles and pore water (collected by syringe) were placed in an argon-filled glove box; residual sediment was set aside.

All pore water samples were filtered through 0.45 μm syringe filters into one of four aliquots. The first aliquot was placed into clean 20-mL glass liquid scintillation vials, removed from the glove box, sealed, chilled, and submitted for anion analysis by IC (Sect. 3.4). The second aliquot was placed into a cleaned beaker, removed from the glove box, and titrated by ultrapure 0.1 *N* HCl (Ultrix) to determine the alkalinity; as with surface water samples, preserved samples were submitted for ICP scan (Sect. 3.4). A third aliquot was filtered directly into an acid-cleaned, 15-mL polyethylene bottle, and sealed while still in the glove box to reduce exposure to the air. This sample was frozen until analysis for As(III) could be performed (Sect. 3.5). After analysis for As(III), the sample was acidified with 6 *M* ultrapure HCl for total inorganic arsenic determination; As(V) was determined by difference between the total inorganic arsenic and As(III) results.

Residual sediment solids were removed from the glove box, weighed, and oven dried at 60°C for 24 to 48 h. Dried samples were then reweighed to determine the percent moisture of each section. Solids were submitted for ICP metals analysis to determine As, Fe, and Mn values, reported in $\mu\text{g/g}$ dry weight. Using analyte concentrations, sediment wet and dry weight information, and a sediment density estimate (1.3 g/cm^3), sediment porosities (in cubic centimeters per gram) were calculated using the following equation:

$$\text{Porosity (cm}^3\text{/g)} = \% \text{H}_2\text{O}_{\text{sediment}} / [\% \text{H}_2\text{O}_{\text{sediment}} + (100 - \% \text{H}_2\text{O}_{\text{sediment}})/\phi]$$

where ϕ is the sediment density; the units for this convert directly into liters per kilogram. This calculation facilitated the conversion from mass of constituent per mass of sediment dry weight to moles of constituent per mass of sediment dry weight, using the following equation:

$$\text{As solids (}\mu\text{mole/L)} = \text{As}(\mu\text{g/kg}) / (\text{porosity (L/kg)} \times 1 \mu\text{mole/74.92135 } \mu\text{g})$$

These values were used to calculate K_D for specific contaminants, by dividing the solid value by the pore water value. Porosity data are included in Volume 2 (Table 5).

3.4 STANDARD LABORATORY ANALYSES

Chilled water and pore water samples were submitted for major ion analysis (including bromide, chloride, fluoride, nitrate-nitrite nitrogen, and sulfate) by IC (EPA method 300.0, EPA 1986a) and total organic carbon (SW-846 9060, 1986b). Preserved water and pore water samples were submitted for analysis of metal constituents, primarily As, Ca, Fe, Mg, and Mn

by ICP (SW-846 method 6010, EPA 1986b). Bulk sediment solid samples also were submitted for ICP metals analysis, focusing on As, Fe, and Mn. Analyses were performed by either the ORNL Analytical Chemistry Division or the K-25 Site Technical Division's Analytical Chemistry Department. Bulk sediment solids were submitted for arsenic analysis only for the August 1990 sampling event; determination of As, Fe, and Mn in bulk sediments was requested for all other sediment sampling events. Analyses for NPDES monitoring for NPDES permit number TN0002941 at outfall 302 followed standard protocols. A description of the NPDES monitoring program and an annual summary of monitoring results may be found in the ORR Environmental Monitoring reports for 1990 (Kornegay et al. 1991), 1991 (Kornegay et al. 1992), 1992 (Kornegay et al. 1993), and 1993 (Kornegay et al. 1994). The reporting limit for NPDES arsenic data is approximately 530 nM.

3.5 ARSENIC SPECIATION ANALYSIS

Analysis of surface water and sediment pore water samples for arsenic speciation was performed by hydride generation atomic absorption spectrophotometry (HGAAS) (Andreae 1983); speciation determination was not performed on bulk sediment solid samples. This method combines hydride generation with cryogenic trapping and concentration before introduction into the atomic absorption spectrophotometer. This method results in absolute detection limits of 1 to 2 picomoles, or 0.02 to 0.04 nM (1.5 to 3 ng/L) for a 50-mL sample. Briefly, the arsenic species in the sample are converted to their corresponding hydrides by reduction with sodium borohydride, stripped from solution with a stream of helium, and trapped on chromatographic column submerged in liquid nitrogen. After all hydrides have been stripped and trapped, the liquid nitrogen is removed, and the trap is warmed. The hydrides elute in order of boiling point into a hydrogen flame contained in a quartz tube burner. The burner is aligned in the light path of the spectrophotometer (Buck Scientific, Model 200) at a wavelength of 193.7 nm. The chromatographic separation is sufficient to differentiate the methyl arsenic species from the inorganic species. The output of the spectrophotometer was transformed with an analog to digital (A/D) converter, and peak areas were electronically integrated.

Oxidation-reduction speciation is accomplished by controlling the reduction reaction conditions. Arsenite [As(III)] is analyzed by buffering the pH at 6. Only As(III) reacts at this pH. A separate aliquot is analyzed at a pH of 1, where both As(V) and As(III) are reduced to arsine, and reported as total inorganic arsenic. Arsenate [As(V)] concentrations are calculated by difference of the pH 6 and pH 1 analyses as follows:

$$\text{As(V)} = \text{total inorganic As} - \text{As(III)}$$

in nM.

Quality control (QC) for the arsenic speciation analysis consisted of replicate analyses of samples and standards, analysis of field blanks, analysis of field duplicate samples, analysis of certified standards for accuracy, and analysis of in-house standards for determination of sensitivity. QC results are presented in Volume 2.

3.6 DATA MANAGEMENT

Field data, including collection-event-specific information, water quality data, alkalinity data, and sediment weight data, were entered into Lotus 1-2-3 spreadsheets (Lotus Development Corporation 1994) following sample collection. Hard copy analytical data were reviewed and added to the spreadsheet information. Original hard copies of all field and laboratory data, as well as all field and laboratory notes, are kept in CR-ERP project records. Spreadsheet copies of these data were included in a CR-ERP electronic database, initially in Statistical Analysis Systems (SAS) datasets on mainframe computers, and were migrated with the other CR-ERP data to the CR-ERP workstation. A formal, controlled tracking form was completed containing information about each arsenic sample collected, including the analyses requested. Hard copy and electronic data were used to ensure that the appropriate information about each sample was recorded in the database and that the proper analytical results were expected and received back from the laboratories. Statistical analyses on all data were performed using SAS version 6.10 for Unix workstations (SAS Institute 1993); analyses included determination of the extent to which the data departed from a normal distribution, analysis of variance (using the general linear model procedure) for classification variables (site, depth season), and multiple F-tests of significant differences ($\alpha = 0.05$) between classification variables; for these tests, the alpha level was set to 0.05 or 95%. Graphical presentations of the data were prepared using SigmaPlot graphics (Jandel Scientific 1993) and Harvard Graphics (Harvard Graphics 1994).

3.7 QUALITY ASSURANCE/QUALITY CONTROL

Quality assurance/quality control (QA/QC) for this project consisted of collection of samples to meet the objectives specified in Sect. 1.3. Specifically, these objectives were met through collection of field duplicate samples, equipment rinse blanks, and rigorous calibration of equipment. QC samples were collected for approximately 5% of all samples collected. QC sample submittals were most rigorous during the last year of this study, corresponding to the establishment of formal, controlled tracking forms. Data validation for this report consisted of assessment of analytical QC data, assessment of chemical charge balances for major ion data, review of all data for outliers, and consistency with other comparable results. Data evaluation is summarized in Volume 2.

Equipment rinse blank samples were used to evaluate the adequacy of equipment cleaning procedures for the specified analyses. Additional evidence of the cleanliness of equipment may be derived from arsenic speciation results, where extremely small quantities of contamination would result in consistently spurious readings. Duplicate samples were collected to assess the short-term representativeness of the samples. Samples collected at the same time, under identical conditions, and submitted for the same analyses were compared using relative percent difference (RPD) criteria, as presented in Volume 2.

Additional QC measures included the calculation of the ionic charge balance. This balance is one-to-one in all chemical systems. Charge balance is calculated to determine if the analytical results have adequately characterized all major ions. This balance is the molar ratio of the number of positive (cation) to negative (anion) chemical charges in a sample. Deviations of more than 20% from a one-to-one ratio indicate a possible problem with the chemical results; either a result was spurious or a major ion was not accounted for by the requested analyses. Charge balance was also used to eliminate those ions from analysis that

did not contribute significantly to the charge-balance, thus saving analytical costs. Charge balance data are summarized in Volume 2.

Chain of custody was maintained for all samples collected for this project, following guidelines established for environmental restoration work on the ORR (Kimbrough et al. 1990). Using sequentially numbered forms, the field team initiated custody at the time of sample collection. Sample tracking information was recorded on the forms, which became part of the daily record. Unique identification numbers were assigned to all samples at the time of collection, and custody seals were used to ensure the integrity of the samples. Custody was transferred to the analytical laboratories receiving the samples. Custody was maintained by access controls for all samples processed and analyzed by the co-authors and CR-ERP staff. All QA/QC data for this project are presented in Volume 2.

3.8 QUALITY ASSURANCE/QUALITY CONTROL SUMMARY

This section is taken from Chap. 5 of the Quality Assurance/Quality Control Summary Report for this study, which is attached to this document as Volume 2. The purpose of this section is to evaluate the QA/QC results for this study, in terms of both the project's objectives (see Sect 1.3) and the standard precision, accuracy, representativeness, sensitivity, comparability, and completeness objectives, as appropriate. For the first, third, and fourth quality objectives from Sect. 1.3—routinely obtaining very low analytical detection limits for arsenic speciation in the CR/WBR system—values presented in Tables 4, 5, and 6 of Volume 2 indicate that the required detection limits were obtained for all arsenic speciation samples. It should be noted that detection limit values for standard analytical methodologies ($1 \mu\text{g/L}$ or 13 nM) are much larger than the values reported routinely from arsenic speciation.

Assessment of the third project objective (Sect. 1.3) must include a discussion of (1) sample preservation and (2) analytical holding times issues. Section 3.1 of Volume 2 notes that many samples did not meet the requirement that samples be preserved to less than pH 2. In the future, this preservation issue might be solved by either defining analytical requirements more carefully or using a more concentrated acid preservative following alkalinity titration. Regarding analytical holding times, as is noted in Sect. 3.1 of Volume 2, failure to meet the specified analytical holding times for ion chromatography samples suggests that a great deal of caution should be exercised with these data.

The evaluation of the precision, accuracy, representativeness, sensitivity, comparability, and completeness parameters follows. (1) Precision objectives, evaluated through the use of field and laboratory duplicates, for analytical precision of less than 20% RPD have been met (see Tables 2, 3, and 4 in Volume 2). (2) Accuracy objectives of $\pm 25\%$ recovery for matrix spikes and $\pm 20\%$ for laboratory control samples (LCSs), assessed by reviewing the results of LCSs and matrix spike samples, have been met. (3) Quantitative measures of representativeness, including the use of SOPs, equipment rinse blanks, analytical method blanks, proper preservation, standard analytical methods, and adherence to holding times, were not met for either the samples for ICP analysis documented as having a sample pH greater than 2 or the samples for IC analysis documented as being outside of holding times. (4) The completeness objective, to determine temporal-spatial changes in arsenic concentrations and seasonal changes in water distribution coefficients (K_d) for arsenic and metals, was met when sediment samples had been collected from each of the major sampling sites during each season. (5) Comparability, ensured by the use of similar methods for

sampling and analysis, was met for all samples. (6) Analytical sensitivity was ensured by use of ultra-low arsenic detection methodologies and consistently using comparable methods for different sampling events.

As a further expansion on the evaluation of the completeness objective, the observational approach was used. Using the observational approach to focus sampling efforts, initial investigations were made at secondary sites to identify additional sources or sinks for contamination in the CR/WBR system; data were collected and analyzed from these secondary sources once, and the data were evaluated relative to the project objectives, particularly considering the potential contribution of the site to better characterizing arsenic distribution in the CR/WBR system. If conditions observed at the site were unique from those at adjacent sites and sufficient project resources existed to further characterize the site, it was included in future sampling events. If either of the two conditions was not observed for the site, they were not investigated further, and data from the sites were combined with those for similar adjacent sites.

4. RESULTS

Initially, results will be presented by site for both water column and sediment phases over time; relationships and comparisons among sites will follow. The sites sampled are shown in Fig. 2, and their frequency of sampling is summarized in Table 1. Data are presented in a series of figures. Surface water results, including water temperature, DO, and concentrations of arsenic species (from HGAAS) are presented in Appendix B. Pore water and sediment solids results, including concentrations of arsenic species by HGAAS and distribution coefficients (K_D) for As, Fe, and Mn, are presented in Appendix B in Volume 2. The results of statistically conservative ($\alpha = 0.05$) significance tests between sites, depths, and seasons are presented in a series of tables.

4.1 LOWER WATTS BAR RESERVOIR

Surface water from three sites in LWBR (TRK 849.6, TRK 863.2, TRK 875.2), initially sampled to characterize conditions there (Table 1), showed low levels of arsenic (Appendix A in Volume 2). Surface water sampling at TRK 863.2 and TRK 875.2 was discontinued after January 1991, using the criteria listed in Sect. 3.8; results from these sites are combined with TRK 849.6 for the remainder of this presentation. Water column conditions, specifically water column stratification and DO content, varied seasonally for LWBR; higher water temperatures and lower DO contents were observed during the summer compared with other seasons (Fig. 3¹, Appendix A in Volume 2). During winter and spring, water temperatures and DO values were uniform from top to bottom; total inorganic arsenic levels, predominately As(V), were consistently less than 3.5 nM and did not vary significantly throughout the water column (Fig. 4, Appendix A in Volume 2, Table 2). Winter sediment pore water arsenic values were low near the surface sediment (10 to 15 nM), increasing by a factor of 10 a few centimeters deeper in the sediment (Fig. 5, Appendix B in Volume 2, Table 3).

Summer water column stratification, indicated by rapid and large changes in DO and temperature values, was observed (Fig. 3, Appendix A in Volume 2). Arsenic values in the upper water column (1.5 to 4 nM) were similar in magnitude to those observed during the winter, but were significantly higher (5 to 9 nM) near the sediment-water interface (Fig. 4, Tables 2 and 7). Arsenate [As(V)] was the predominant form found either in surface water or pore water (Appendixes A and B in Volume 2). Fall DO and temperature values were more uniform throughout the water column, with no evidence of water column stratification (Fig. 3). Fall arsenic values were uniform throughout the water column, with values comparable to those observed deep during summer (Appendix A in Volume 2, Fig. 4). However, sediment pore water values near the sediment-water interface were intermediate between summer and winter and lower than winter or summer at depth (Fig. 5, Appendix B in Volume 2).

Values for spring arsenic K_D were significantly greater than for summer or fall (Appendix B in Volume 2, Table 4); fall Fe K_D s were significantly higher than other seasons (Table 5). Summer arsenic K_D s were significantly higher for surface sediments and decreased with depth in all seasons (Appendix B in Volume 2, Table 4). The K_D s for Mn did not change

¹Figures and tables that are called out in this chapter appear at the end of the chapter.

significantly with season (Table 5). Marked changes in surface water arsenic levels were observed both from winter to summer and with water column depth in the summer (Fig. 4, Appendix A in Volume 2, Tables 6 and 7). Pore water arsenic values were much greater (two to three times) in the top 18 cm of sediment during summer as opposed to winter or spring (Fig. 5, Appendix B in Volume 2); below 18 cm, pore water arsenic values were very similar regardless of season.

4.2 KINGSTON

Water column conditions for temperature and DO varied seasonally at the Kingston site. Winter-spring temperatures ranged between 10 and 15°C, with the warmest values at the surface (0 to 0.5 m depth) [Fig. 6(a and b)]. DO values were uniform throughout the water column (Fig. 6). Highest water column arsenic values in the winter and spring were observed near the water surface, ranging from 6 to 20 nM [Fig. 7(a and b), Appendix A in Volume 2]. Values dropped with depth in the water column. Pore water arsenic values were low (<30 nM) near the surface sediments, increasing greatly with depth in the sediment; maximum values ranged between 600 and 800 nM (Fig. 8, Appendix B in Volume 2).

Summer water temperatures ranged from 25 to 29°C at the surface, dropping to between 21 and 23°C at a depth of 6 m (Fig. 6, Appendix A in Volume 2). DO values were near saturation at the surface and did not drop below 70% deeper in the water column (Fig. 6). Surface water arsenic values were elevated from 0 to 2 m deep, consistently showing maximum values ranging from 15 to 20 nM [Fig. 7(c), Appendix A in Volume 2]. Arsenic concentrations were higher overall (Table 2), and significantly higher during summer, at 0.5 m than they were deeper in the water column (Table 12). At depth, from 6 m to the bottom, the arsenic values dropped to 5 nM or less. Pore water arsenic values were similar to those observed in winter and spring, with lower values at the sediment surface, increasing greatly with depth in the sediment (Fig. 8, Appendix B in Volume 2).

During fall, water column temperature and DO conditions were relatively uniform, with a slight depression of temperature at the surface and a corresponding increase in DO values (Fig. 6, Appendix A in Volume 2). Surface water inorganic arsenic values were near 20 nM and decreased consistently with depth, reflecting summer values (Appendix A in Volume 2). Pore water inorganic arsenic was two to four times greater in surface sediments than observed for other seasons (Fig. 8, Appendix B in Volume 2). Differences with season were not significant (Table 8). Values for sediment pore water were significantly lower in fall than for spring or summer (Appendix B in Volume 2, Table 9). Sediment pore water values in spring and summer were significantly higher than for fall and winter (Table 9). Arsenic, Fe and Mn K_D values were not significantly different across all seasons (Appendix B in Volume 2, Table 5). Highest K_D values were found at the sediment surface.

Surface water arsenic concentrations for several sites in the Kingston area were significantly higher immediately upstream (CRK 5.6) and downstream (CRK 4) from the Kingston Steam Plant outfall than at other sites, including TRK 907.2, CRK 1.6, CRK 8, and PCK 1.6 [Fig. 7(a-c), Appendix A in Volume 2, Table 10]. Summer and fall values were also significantly higher than in winter and spring (Table 6). Highest inorganic arsenic values during winter, spring, and summer were observed at the CRK 4, CRK 5.6, and CRK 1.6 sites [Fig. 7(a-c), Table 11]. Differences between this group and the other sites (CRK 8 and TRK 907.2) were significant during summer for As(V), though not for As(III) (Table 11). As(V)

values in the upper 1 m of the water column were higher than those deeper in the water column for these sites during all seasons, though only summer values were significantly greater (Table 12). As(III) values were also significantly higher in the top 1 m of surface water during the summer; however, highest values for As(III) were observed near the sediment-water interface during winter (Table 12). For each of the previous comparisons, values for surface water in the Kingston area are greater than observed in Poplar Creek or lower Watts Bar (Tables 13 and 14).

4.3 POPLAR CREEK

Water column temperatures reflected normal seasonal patterns, though DO changed little with season, and the water column was not stratified (Fig. 6, Appendix A in Volume 2). Inorganic arsenic values during winter and spring (average 1.8 nM) were significantly lower than summer (average 6 nM) or fall (average 4 nM) [Fig. 7(a-c), Table 6]. The 9-nM arsenic value at 5 m deep in the water column, significantly greater than other water column depths, was observed during the summer (Appendix A in Volume 2, Table 12). Values were uniform throughout the water column for all other seasons (Appendix A in Volume 2). Values at the main Poplar Creek site (PCK 1.6) were significantly lower than for sites downstream in the Clinch (Table 13).

Arsenic values for sediment pore water ranged from 150 nM at the surface to between 40,000 and 80,000 nM below 20 cm (Fig. 9, Appendix B in Volume 2). Though As(V) was the predominate form in the surface sediments, As(III) levels were 3 to 5 times higher than As(V) in deeper sediments. Winter and summer As(III) values were significantly higher than fall and spring, while no significant differences were observed among seasons for As(V) (Table 15). Arsenic K_D values were significantly higher for surface sediments than deep sediments, though no seasonal changes were observed (Appendix B in Volume 2, Tables 16 and 17). The Fe and Mn K_D values did not vary significantly with season or depth in the sediment. Pore water arsenic levels in surface sediments (1.5 to 4.5 cm) were significantly lower than deep sediments for all seasons (Table 18). The surface sediments were in the same range as, and not significantly different from, other sites, including LWBR and Kingston (Appendix B in Volume 2, Table 19). Concentrations of arsenic in surface sediments did not change with season (Table 20); they were significantly lower than other sites in summer and higher in winter (Table 21).

4.4 MELTON HILL RESERVOIR AND LOWER McCOY BRANCH EMBAYMENT

Water temperature values reflected normal seasonal changes with no differences between the sites in the LMBE area and in Melton Hill Reservoir at CRK 60.5, immediately adjacent to LMBE [Fig. 10(a-b), Appendix A in Volume 2]. DO values were stable for all seasons, sites, and depths at MBK 0.3 (Fig 11). Water column arsenic values combined for all sites did not change significantly over season (Table 6). Surface water arsenic levels at MCBK 0.3 were highest in summer; no significant differences were observed with water column depth (Tables 2 and 6). Surface water inorganic arsenic values at MCBK 0.5 were not significantly different with season or with water column depth; however, summer As(III) levels were significantly higher than either winter or spring. Spring As(V) values were higher than winter (Tables 2 and 6). Arsenite [As(III)] values for 4 m deep in the water column, near the sediment-water interface, were significantly higher than for all other depths (Table 12). The highest site-

specific values were observed for MCBK 0.5 (average 14 nM), followed by MCBK 0.3 (average 6 nM), and the Melton Hill reservoir site (CRK 60.5, average 2.7 nM) [Fig. 12(a-c)]. Differences between these sites were significant (Table 10). Trends in arsenic concentrations over water column depth in the LMBE area were not significant (Table 2). Differences between CRK 60.5 and MCBK 0.3 were not significant in winter and spring (Tables 10 and 11). Winter and spring arsenic concentrations in LMBE were highest at the water surface for MCBK 0.5, declining with depth and distance downstream [Fig. 12(a-c), Tables 2 and 10]. Summer values were significantly higher for bottom water (4 to 5 m) than for intermediate depths (2 to 3 m), though they were not significantly different from upper portions of the water column (0.5 to 1 m) [Table 12, Fig. 12(a-c)].

Sediment pore water arsenic values for the MCBK 0.5 site was greater than MCBK 0.3, and both were significantly greater than CRK 60.5 (Table 22). No significant differences were observed for the LMBE area as a whole, either with season or depth in the sediment (Tables 23 and 24). Pore water values were significantly higher in summer at MCBK 0.5 than at the other sites (Table 25), while winter values were significantly higher at MCBK 0.3 than at either MCBK 0.5 or CRK 60.5 (Table 25). Surface sediment values were greater in the summer and fall than during the winter or spring (Appendix B in Volume 2, Table 26). Particle-to-water distribution coefficients for As, Fe, and Mn did not change significantly between sites, seasons, or sediment depths (Tables 27 and 28). Values for As and Mn K_{ps} were higher for surface sediments in summer and winter than they were for fall, though Fe K_{ps} for winter surface sediments (1.5 cm) were significantly higher than for sediments deeper than 1.5 cm (Table 29). Highest K_p values were observed in fall (Appendix B in Volume 2). Surface sediment arsenic concentrations were similar for all sites during all seasons in LMBE (Table 30). Surface sediment values were significantly lower than observed in UMBE during summer (Table 19).

Water quality conditions for the limited number of observations available near the BRSP indicated that while the downstream portions of this area were thermally stratified in summer, the stratified zone was replaced by riverine conditions of uniform water column temperature and DO values immediately upstream from the BRSP (Appendix A in Volume 2). No significant differences in arsenic were observed among sites, seasons, or with water column depth (Tables 2, 6, and 10). The maximum levels of inorganic arsenic in the BRSP area were approximately 4.5 nM at CRK 73.6, with levels higher in surface waters than at depth (Appendix A in Volume 2). No sediment or sediment pore water samples were collected for this site.

4.5 UPPER MCCOY BRANCH EMBAYMENT AND ROGERS QUARRY

Winter water temperatures (6.7°C), and DO levels (91% saturation) were consistent with depth in UMBE [Fig. 10(a)]. Summer surface water conditions in UMBE were similar at all sites, with water temperatures ranging between 24 and 26°C for the top 3 to 4 m; a zone of rapid temperature change was observed from 4 to 6 m, with water temperatures cooling to 22°C below 4 m [Fig. 10(b)]. DO values declined with depth, with notable oxygen depletion to below 50% saturation near the sediment-water interface [Fig. 10(b)]. A water column temperature and DO profile for RQ, collected in conjunction with the June 1992 sampling, indicated a surface water mixed layer, a thermocline extending 6 to 12 m and an extensive hypolimnion below 12 m deep (Appendix A in Volume 2). There was a deep DO peak (160%

saturation) below the thermocline, with DO values falling below 50% saturation near the sediment-water interface.

Summer inorganic arsenic values at MCBK 0.7 increased by an order of magnitude with depth in the water column, with a similar increase in As(III) [Fig. 12(c), Appendix A in Volume 2]. Average surface water arsenic values were two to four times lower in winter than during summer (Appendix A in Volume 2). Average values were lower for winter (25 nM) and spring (55 nM) as compared to summer (65 nM). However, As(III) values for summer (average 3.3 nM) were significantly greater than for winter (average 0.7 nM, Table 6). The summer water column inorganic arsenic values in UMBE were near 100 nM [Fig. 12(c)]. RQ arsenic values were significantly higher for the outfall at MCBK 1.6 (average 220 nM) and in the body of RQ at MCBK 1.8 (average 170 nM) than at the MCBK 2 site feeding into the quarry (average 35 nM, Table 10). There were no significant seasonal changes in arsenic for the RQ outfall [Fig. 13(a), Table 6]. For a single sample collection in RQ, inorganic arsenic increased greatly with depth in the water, from 140 nM near the surface to 400 nM near the bottom, corresponding to temperature and DO changes in the water column (Appendix A in Volume 2).

Analysis of weekly arsenic speciation samples from RQ yielded consistently lower values for inflow as compared to outflow. Weekly arsenic data from sampling associated with NPDES outfall #302 at MCBK 1.6 for March 1990 through April 1993 show a drop in total arsenic values from 1070 nM to 530 nM [Fig 13(a)]. The majority of the decline occurred during 1990; for subsequent years, values exceeded the minimum NPDES reported level of 530 nM only during November 1991. Turbidity values also decreased from an average of 1.9 NTU in 1990 to 0.9 NTU in 1993 [Fig. 13(b)]. For 1992 and 1993, values greater than 2 NTU were observed only during winter and spring. Monitored pH values were highest during spring and summer of 1990 and 1991, with maxima of 9 and 9.2 for each year [Fig. 13(b)]. Maximum values were lower in 1992 (8.6) and 1993 (8.1). COD was highest during spring and summer, dropping to the minimum reported value (5 mg/L) during fall and winter [Fig. 13(b)]. Water flows were highest during the winter and spring (1.5 to 2 cfs) during all years, dropping to base flow values (0.03 cfs) during summer and fall [Fig. 13(b)]. These data are summarized in the Oak Ridge Reservation Environmental Monitoring reports for 1990 (Kornegay et al. 1991), 1991 (Kornegay et al. 1992), 1992 (Kornegay et al. 1993), and 1993 (Kornegay et al. 1994).

Pore water inorganic arsenic values were consistently greater than 4000 nM at MCBK 0.7 during summer, while a sharp gradient in pore water arsenic from 1500 nM near the sediment surface to 7000 nM by 40 cm in the sediment was observed at MCBK 0.85 (Figs. 14 and 15); both As(III) and As(V) were observed in roughly equal proportions (Appendix B in Volume 2). Average summer values were significantly greater than average winter values for all arsenic species in UMBE (Table 31). Summer pore water arsenic values were 3 to 50 times greater in the UMBE surface sediments than for surface sediments at any other site (Appendix B in Volume 2, Table 19). The gradient of increasing pore water arsenic with depth, observed at all other sites, was not present at MCBK 0.7 (Fig. 14); values did decrease with depth at MCBK 0.85, but surface pore water arsenic was still greater than for all sites outside of UMBE (Appendix B in Volume 2, Tables 19 and 32, Fig 15). Pore water inorganic arsenic in UMBE was primarily As(V), though the proportion of As(III) was higher than for surface sediments at all other sites (Table 19). Pore water arsenic values for surface sediments (<5 cm deep) in UMBE were significantly greater at 4.5 cm and 5 times greater at 1.5 cm for UMBE than for Poplar Creek (Appendix B in Volume 2, Table 21, Figs. 9, 14, and 16);

trends were reversed for winter (Table 21). Average K_D values for arsenic were significantly higher in winter than summer, though differences were not significant with depth in the sediment for a given season (Tables 28, 33, and 34). Trends for Mn K_D values were similar to those for arsenic, with large seasonal changes and no significant difference over depth in the sediment. Iron K_D values did not differ significantly over season, though surface values were significantly higher than those at depth (Tables 28 and 33).

Surface water concentrations of inorganic arsenic in the McCoy Branch Embayment area were significantly higher at the RQ outfall than at any other site during all seasons (Table 13). Additionally, arsenic levels in UMBE (MCBK 0.85 and MCBK 0.7) were significantly higher than in LMBE (MCBK 0.5, MCBK 0.3, and CRK 60.5) (Table 13). Sediment K_D values for As, Fe, and Mn did not differ significantly among these UMBE sites during fall, spring, or winter (Table 28).

4.6 SPATIAL-TEMPORAL COMPARISONS

Mean winter surface water arsenic concentrations, with the exception of RQ, were higher in UMBE (average 25 nM) than in the other study areas (Table 35). However, winter As(III) values for the RQ outfall (average 0.7 nM) were not significantly different from UMBE (average 0.73 nM), Poplar Creek (average 0.21 nM), or LMBE (average 0.19 nM) sites (Table 36). Average pore water arsenic concentrations for all depths were significantly greater in Poplar Creek (average 38,000 nM) than for any other study area (Table 37). There were no significant differences in Fe K_D values between any of the study sites (Table 38).

Spring total inorganic arsenic concentrations were significantly higher in UMBE (average 55 nM) than all other sites, excluding the RQ outfall (average 221 nM) (Table 36). Average inorganic arsenic pore water values were greatest in Poplar Creek (average 31,000 nM), with As(III) comprising 75% of the inorganic arsenic total and average pore water values 10 to 100 times greater than for all other sites (Table 37). Arsenic and Fe K_D values, only evaluated for the Poplar Creek and LWBR sites during spring, showed no significant difference between sites or depths in the sediment, though there was a wide range of values for each site (Appendix B in Volume 2). Manganese K_D values were significantly higher for Poplar Creek and lower Watts Bar as compared to Kingston; no significant differences were observed with sediment depth.

As in other seasons, UMBE had significantly higher total inorganic arsenic levels during summer (average 65 nM) than other sites, excluding the RQ outfall (average 244.9 nM) (Table 13). Surface water inorganic arsenic values were also significantly higher at Kingston and LMBE than at Poplar Creek, BRSP, or LWBR (Table 36). Average pore water inorganic arsenic values for Poplar Creek were significantly higher than all other sites, followed by UMBE, LMBE, Kingston, and LWBR (Table 37). Pore water arsenic K_D values for UMBE were lower than all other sites; differences were only significant between LWBR and UMBE (Table 38). No significant differences in As or Mn K_D were observed with depth in the sediment. Iron K_D values were not different between sites, but were higher at the sediment surface, compared to deep sediments across all study areas (Appendix B in Volume 2). Manganese K_D values for LMBE, Kingston, and LWBR were lower than those observed for both Poplar Creek and UMBE (Table 38).

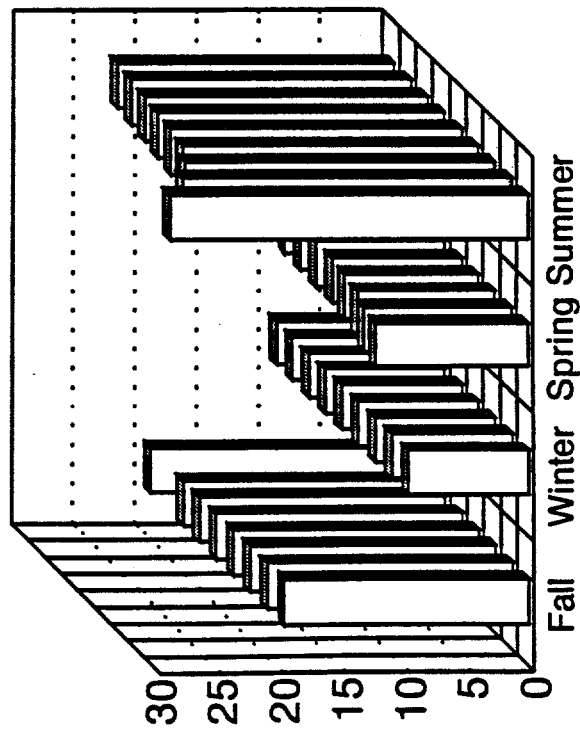
An insufficient number of fall visits were made to perform statistical comparisons on inorganic arsenic between sites. Trends in surface water and sediment pore water arsenic were similar to those observed for other seasons (Appendixes A and B in Volume 2). There were no notable trends observed across sites or with depth for sediment As, Fe, or Mn K_D values.

4.7 RISK SCREENING CRITERIA FOR SURFACE WATER DATA

Arsenate concentrations greater than or equal to 60 nM for carcinogenesis and 146 nM for toxicity, which exceed human health risk screening criteria, as well as concentrations greater than 108 nM for As(V), which exceed an ecological risk benchmark criterion (Tier II secondary chronic value, Suter and Mabry 1994) were observed for surface waters during this study. Because of the extreme chemical conditions that exist in sediment pore waters, screening criteria are not applied to pore water data. Risk screening criteria were only exceeded for surface water in RQ and UMBE.

Surface water samples from RQ and UMBE exceeded the As(V) ecological and both human health screening concentrations at least once. All RQ outfall results [Fig. 13(a)] exceed these criteria. The summer 1992 UMBE surface water samples collected from MCBK 0.7 also exceeded both human health and ecological risk screening criteria [Fig. 12(b)].

Temperature (degrees C)



Dissolved Oxygen (% saturation)

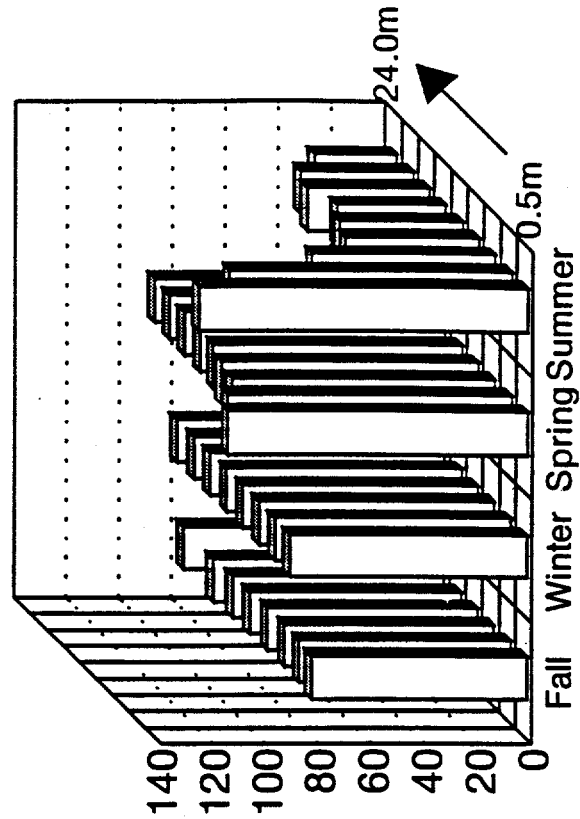


Fig. 3. Bar charts of water temperature (degrees C) and dissolved oxygen (% saturation) with season and depth in lower Watts Bar Reservoir (TRK 849.6).

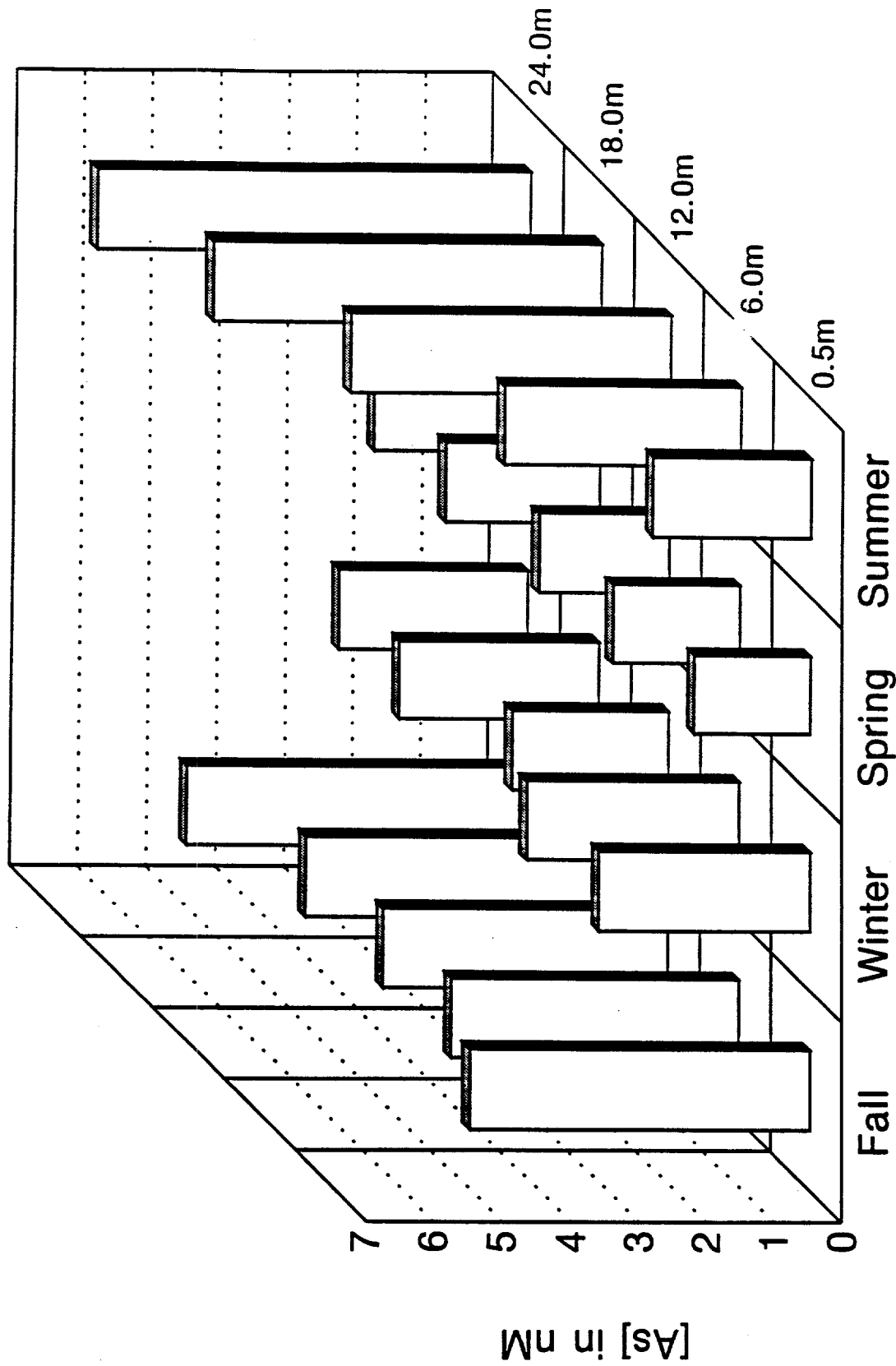


Fig. 4. Bar chart of total dissolved inorganic arsenic (nM) with season and depth for surface water in lower Watts Bar Reservoir (TRK 849.6).

Table 2. The mean inorganic As, AsIII, and AsV concentrations ($\mu\text{g/L}$) of each source by depth^a

Depth (m)	N	Mean Inorganic As (Group)	Mean AsIII (Group)	Mean AsV (Group)
Lower Watts Bar Reservoir				
0.5	12	2.56 (C)	0.14 (C)	2.42 (A)
3.0	13	2.68 (C)	0.13 (C)	2.55 (A)
6.0	13	2.89 (BC)	0.25 (C)	2.64 (A)
9.0	13	3.28 (BC)	0.23 (C)	3.05 (A)
12.0	10	3.24 (BC)	0.24 (C)	3.00 (A)
15.0	10	3.84 (BC)	0.19 (C)	3.65 (A)
18.0	10	4.08 (BC)	0.18 (C)	3.90 (A)
21.0	9	4.32 (BC)	0.24 (C)	4.08 (A)
24.0	8	4.77 (ABC)	0.26 (C)	4.51 (AB)
25.0	3	7.04 (A)	0.34 (AB)	6.69 (A)
26.0	2	5.33 (AB)	0.80 (A)	4.53 (AB)
Kingston: CRK 1.6				
0.5	9	13.38 (A)	1.36 (A)	12.02 (A)
3.0	10	7.87 (AB)	0.69 (AB)	7.18 (AB)
6.0	9	5.26 (AB)	0.36 (AB)	4.90 (AB)
9.0	10	4.19 (B)	0.30 (B)	3.89 (B)
12.0	4	4.57 (B)	0.41 (AB)	4.16 (AB)
Poplar Creek: PCK 1.6				
0.5	7	3.68 (C)	0.21 (B)	3.47 (B)
1.0	5	3.11 (C)	0.00 (B)	3.11 (B)
1.5	1	4.59 (BC)	0.33 (B)	4.26 (B)
2.0	6	3.75 (C)	0.21 (B)	3.54 (B)
3.0	5	3.82 (BC)	0.24 (B)	3.58 (B)
3.5	1	1.38 (D)	0.65 (AB)	0.73 (C)
4.0	4	5.34 (B)	0.41 (AB)	4.93 (B)
4.9	1	9.27 (A)	1.25 (A)	8.02 (A)
5.0	1	8.10 (A)	0.18 (B)	7.92 (A)
Lower McCoy Branch: CRK 60.5				
0.5	5	3.05 (A)	0.18 (ABCD)	2.87 (A)
3.0	3	3.49 (A)	0.28 (AB)	3.21 (A)
6.0	4	2.47 (A)	0.16 (BCD)	2.31 (A)
9.0	3	2.34 (A)	0.08 (D)	2.26 (A)
13.0	3	1.99 (A)	0.09 (CD)	1.90 (A)

Table 2 (continued)

Depth (m)	N	Mean Inorganic As (Group)	Mean AsIII (Group)	Mean AsV (Group)
Lower McCoy Branch: MBK 0.3				
0.5	12	6.22 (A)	0.59 (A)	5.63 (A)
2.0	10	4.93 (A)	0.46 (A)	4.47 (A)
3.0	7	5.15 (A)	0.65 (A)	4.50 (A)
4.0	7	4.16 (A)	0.56 (A)	3.60 (A)
5.0	9	7.77 (A)	1.07 (A)	6.70 (A)
6.0	7	5.67 (A)	0.37 (A)	5.30 (A)
7.0	3	5.15 (A)	0.18 (A)	4.97 (A)
7.5	3	11.57 (A)	1.42 (A)	10.15 (A)
Lower McCoy Branch: MBK 0.5				
0.0	5	15.62 (A)	0.85 (B)	14.77 (A)
0.5	2	7.16 (A)	0.91 (B)	6.25 (A)
2.0	2	7.23 (A)	0.82 (B)	6.41 (A)
4.0	2	23.58 (A)	5.10 (A)	18.48 (A)
Lower McCoy Branch: All sites combined				
0.0	5	15.62 (A)	0.85 (A)	14.77 (A)
0.5	19	5.49 (AB)	0.51 (A)	4.98 (B)
1.0	6	6.63 (AB)	0.54 (A)	6.09 (B)
2.0	13	5.12 (AB)	0.51 (A)	4.61 (B)
3.0	10	4.65 (AB)	0.54 (A)	4.11 (B)
4.0	10	7.87 (AB)	1.43 (A)	6.44 (AB)
5.0	9	7.77 (AB)	1.07 (A)	6.70 (AB)
6.0	11	4.51 (AB)	0.29 (A)	4.22 (B)
Bull Run Steam Plant				
0.0	8	2.99 (A)	0.25 (A)	2.74 (A)
0.5	1	4.53 (A)	1.22 (A)	3.31 (A)
2.0	1	4.52 (A)	1.26 (A)	3.26 (A)
4.0	1	2.00 (A)	0.02 (A)	1.98 (A)
6.0	1	2.02 (A)	0.02 (A)	2.00 (A)
8.0	1	1.84 (A)	0.00 (A)	1.84 (A)
10.0	1	1.83 (A)	0.02 (A)	1.81 (A)
Upper McCoy Branch				
0.0	8	53.53 (A)	1.88 (A)	51.65 (A)
0.5	3	46.50 (A)	3.16 (A)	43.34 (A)
1.0	3	18.70 (A)	1.89 (A)	16.81 (A)
1.5	1	82.10 (A)	7.95 (A)	74.15 (A)
2.0	2	52.11 (A)	4.25 (A)	47.86 (A)
3.0	2	62.70 (A)	9.64 (A)	53.06 (A)

^aDifferent grouping letters (A, B, C, D) indicate significantly different F statistic values at a $p < 0.05$. Groupings are relative to each source.

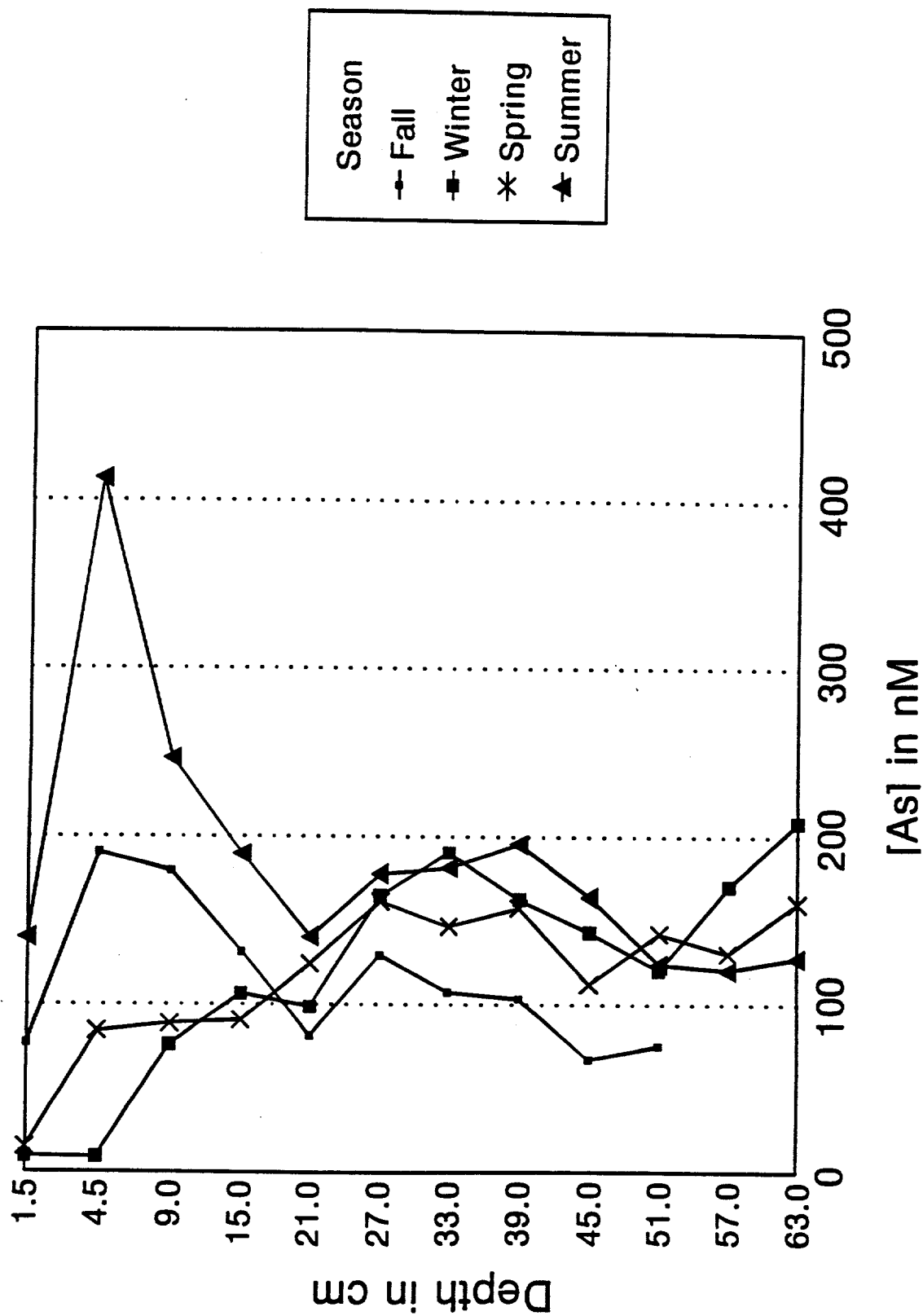


Fig. 5. Profile of total dissolved inorganic arsenic (nM) in pore water by depth in the sediment for each season in lower Watts Bar Reservoir (TRK 849.6).

Table 3. Mean inorganic As, As(III), and As(V) concentrations (nM) for pore water by depth in the sediment from lower Watts Bar Reservoir^a

Depth (cm)	N	Inorganic As	As(III)	As(V)
1.5	6	87	21	66
4.5	6	254	78	176
9.0	6	180	91	93
15.0	6	149	54	95
21.0	6	120	51	69
27.0	6	164	64	100
33.0	6	164	56	108

^aF statistic values for sediment depths are not significantly different at a $p < 0.05$.

Table 4. Mean arsenic, iron, and manganese K_D for each sediment depth in lower Watts Bar Reservoir^a

Summer					All seasons			
Depth (cm)	N	As K_D	N	As K_D	N	Fe K_D	N	Mn K_D
1.5	3	1242 (A)	5	2929 (A)	5	152,280 (A)	5	544 (ABC)
4.5	3	159 (D)	5	580 (A)	5	38,040 (B)	5	276 (BC)
9.0	3	281 (CD)	5	818 (A)	5	12,452 (B)	5	517 (ABC)
15.0	3	407 (BCD)	5	624 (A)	5	11,868 (B)	4	734 (A)
21.0	3	722 (ABCD)	5	1122 (A)	5	8,494 (B)	5	579 (AB)
27.0	3	376 (BCD)	5	560 (A)	5	12,158 (B)	5	292 (ABC)
33.0	3	442 (BCD)	5	689 (A)	5	4,604 (B)	5	194 (BC)

^aDifferent group letters (A, B, C) indicate significantly different F statistic values at a $p < 0.05$.

Table 5. Mean arsenic, iron, and manganese sediment to pore water K_D for each season from lower Watts Bar Reservoir and Kingston^a

Season	Lower Watts Bar Reservoir						Kingston					
	N	As K_D (Group)	Fe K_D (Group)	Mn K_D (Group)	N	As K_D (Group)	N	Fe K_D (Group)	N	Fe K_D (Group)	Mn K_D (Group)	N
Spring	12	2192 (A)	26,579 (AB)	374 (A)	N/A	N/A	9	74,980 (A)	9	282 (A)		
Summer	41	524 (B)	16,218 (B)	303 (A)	24	315 (A)	13	3,248 (A)	13	455 (A)		
Fall	9	627 (B)	38,382 (A)	393 (A)	8	424 (A)	4	68,646 (A)	5	1134 (A)		

^aDifferent group letters (A, B) indicate significantly different F statistic values at a $p < 0.05$.

Table 6. The mean inorganic As, AsIII, and AsV concentrations (nM)
for each source by season¹

Season	N	Mean Inorganic As (Group)	Mean AsIII (Group)	Mean AsV (Group)
Lower Watts Bar Reservoir				
Winter	26	2.96 (B)	0.06 (B)	2.90 (B)
Spring	28	2.00 (C)	0.05 (B)	1.95 (C)
Summer	49	4.41 (A)	0.36 (A)	4.05 (A)
Fall	10	4.66 (A)	0.43 (A)	4.23 (A)
Kingston				
Winter	23	4.89 (B)	0.07 (B)	4.82 (BC)
Spring	24	2.65 (B)	0.05 (B)	2.60 (C)
Summer	33	8.80 (A)	0.97 (A)	7.83 (AB)
Fall	5	9.54 (A)	1.15 (A)	8.39 (A)
Poplar Creek: PCK 1.6				
Winter	9	1.78 (C)	0.22 (A)	1.56 (C)
Spring	3	1.29 (C)	0.00 (A)	1.29 (C)
Summer	15	6.02 (A)	0.34 (A)	5.68 (A)
Fall	4	4.37 (B)	0.41 (A)	3.96 (B)
Lower McCoy Branch: All sites				
Winter	34	5.18 (A)	0.19 (A)	4.99 (A)
Spring	17	4.70 (A)	0.25 (A)	4.45 (A)
Summer	41	8.04 (A)	1.19 (A)	6.85 (A)
Fall	5	3.25 (A)	0.59 (A)	2.66 (A)
Lower McCoy Branch: CRK 60.5				
Winter	6	3.41 (A)	0.03 (B)	3.38 (A)
Spring	4	2.57 (B)	0.24 (A)	2.33 (B)
Summer	11	2.43 (B)	0.21 (A)	2.22 (B)
Lower McCoy Branch: MBK 0.3				
Winter	23	4.94 (AB)	0.25 (B)	4.69 (AB)
Spring	12	3.81 (B)	0.26 (B)	3.55 (B)
Summer	25	8.59 (A)	1.17 (A)	7.42 (A)
Fall	5	3.25 (B)	0.59 (B)	2.66 (B)
Lower McCoy Branch: MBK 0.5				
Winter	5	8.36 (A)	0.11 (B)	8.25 (B)
Spring	1	24.00 (A)	0.18 (B)	23.82 (A)
Summer	5	17.65 (A)	3.43 (A)	14.22 (AB)

Table 6 (continued)

Season	N	Mean Inorganic As (Group)	Mean AsIII (Group)	Mean AsV (Group)
Bull Run Steam Plant				
Winter	2	4.00 (A)	0.06 (A)	3.94 (A)
Spring	3	2.70 (A)	0.36 (A)	2.34 (A)
Summer	9	2.70 (A)	0.38 (A)	2.32 (A)
Upper McCoy Branch: All sites				
Winter	7	25.80 (A)	0.70 (B)	25.10 (A)
Spring	3	55.50 (A)	0.50 (B)	55.00 (A)
Summer	9	65.40 (A)	6.60 (A)	58.80 (A)
Rogers Quarry: MBK 1.6				
Winter	11	188.9 (A)	0.70 (B)	187.30 (A)
Spring	24	221.1 (A)	4.90 (AB)	216.10 (A)
Summer	14	244.9 (A)	17.40 (A)	226.60 (A)
Fall	9	229.4 (A)	0.60 (B)	228.40 (A)
Rogers Quarry: MBK 1.8				
Spring	3	161.0 (B)	1.10 (B)	159.9 (B)
Summer	5	224.4 (A)	2.60 (A)	221.8 (A)
Fall	11	147.8 (B)	0.80 (B)	147.0 (B)
Rogers Quarry: MBK 2.0				
Winter	9	36.50 (AB)	0.20 (B)	36.30 (AB)
Spring	23	37.40 (A)	0.40 (B)	37.00 (A)
Summer	6	40.30 (A)	2.30 (A)	38.00 (A)
Fall	10	28.10 (B)	0.20 (B)	27.90 (B)

^aDifferent grouping letters (A, B, C) indicate significantly different F statistic values at a $p < 0.05$. Groupings are relative to each source.

Table 7. The mean inorganic As, AsIII, and AsV concentrations (nM) from each Watts Bar Reservoir depth by season^a

Season	Depth (m)	N	Mean inorganic As (Group)	Mean AsIII (Group)	Mean AsV (Group)
Winter	0.5	3	3.01 (A)	0.08 (A)	2.93 (A)
	3.0	3	3.18 (A)	0.05 (A)	3.13 (A)
	6.0	3	3.09 (A)	0.06 (A)	3.03 (A)
	9.0	3	3.24 (A)	0.05 (A)	3.19 (A)
	12.0	3	2.09 (A)	0.08 (A)	2.01 (A)
	15.0	3	3.06 (A)	0.07 (A)	2.99 (A)
	18.0	3	3.00 (A)	0.07 (A)	2.93 (A)
	21.0	3	3.11 (A)	0.05 (A)	3.06 (A)
	24.0	1	3.04 (A)	0.04 (A)	3.00 (A)
Spring	0.5	4	1.84 (A)	0.03 (A)	1.81 (A)
	3.0	4	1.85 (A)	0.05 (A)	1.80 (A)
	6.0	4	1.92 (A)	0.06 (A)	1.86 (A)
	9.0	4	1.96 (A)	0.07 (A)	1.89 (A)
	12.0	2	2.08 (A)	0.07 (A)	2.01 (A)
	15.0	2	2.13 (A)	0.07 (A)	2.06 (A)
	18.0	2	2.28 (A)	0.06 (A)	2.22 (A)
	21.0	2	2.29 (A)	0.05 (A)	2.24 (A)
	24.0	2	2.29 (A)	0.01 (A)	2.28 (A)
Summer	0.5	4	2.33 (E)	0.20 (B)	2.13 (D)
	3.0	5	2.69 (CDE)	0.21 (B)	2.48 (CD)
	6.0	5	3.26 (BCDE)	0.49 (B)	2.77 (ABCD)
	9.0	4	4.13 (ABCDE)	0.43 (B)	3.70 (ABCD)
	12.0	4	4.43 (ABCDE)	0.39 (B)	4.04 (ABCD)
	15.0	4	4.98 (ABCDE)	0.31 (B)	4.67 (ABCD)
	18.0	4	5.73 (ABCD)	0.29 (B)	5.44 (ABCD)
	21.0	4	5.88 (ABC)	0.39 (B)	5.49 (ABC)
	24.0	4	6.38 (AB)	0.40 (B)	5.98 (AB)
	25.0	3	7.04 (A)	0.34 (B)	6.70 (A)
	26.0	1	5.39 (ABCDE)	1.01 (A)	4.38 (ABCD)

^aDifferent grouping letters (A, B, C, D, E) indicate significantly different F statistic values at a $p < 0.05$.

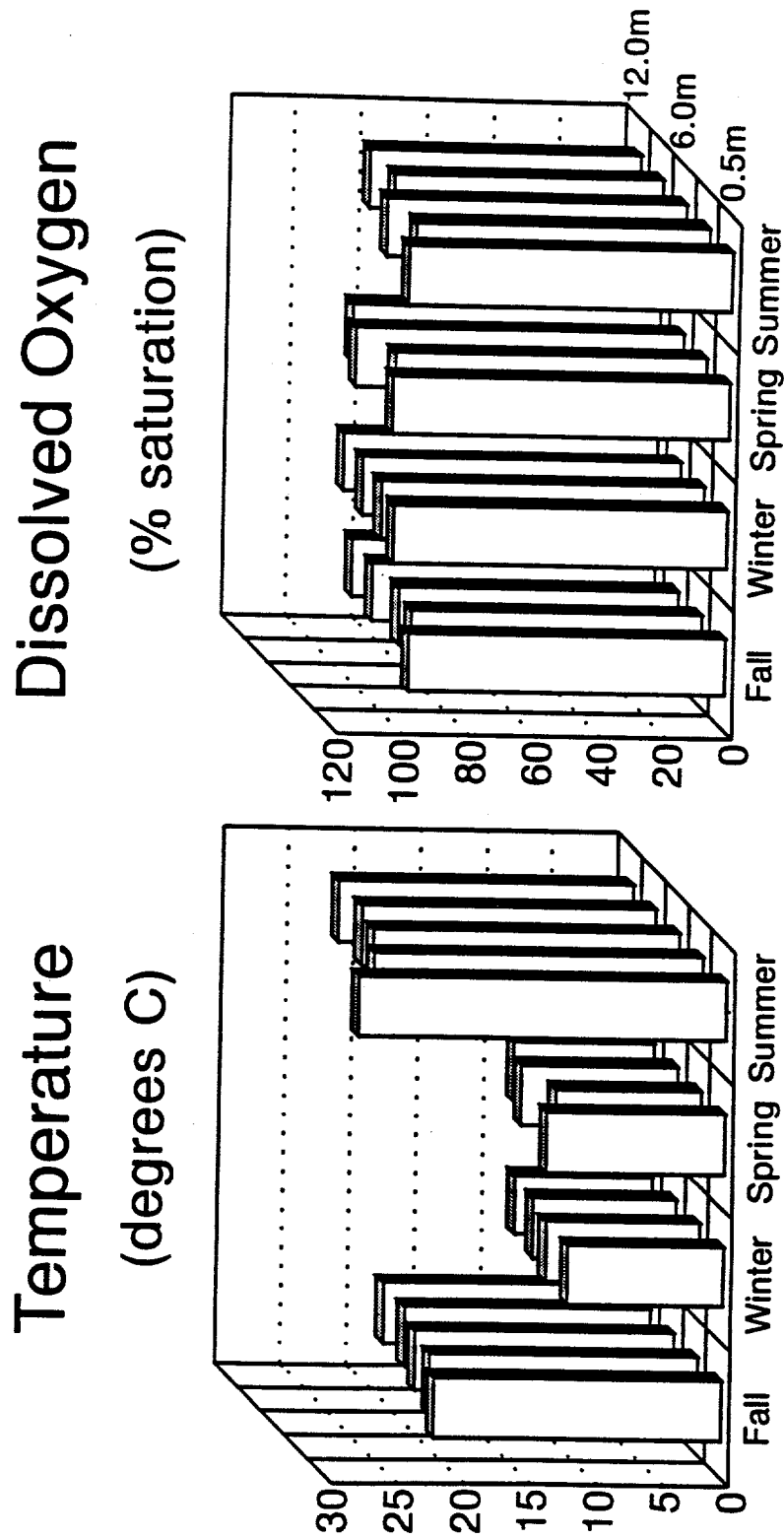


Fig. 6. Bar charts of water temperature (degrees C) and dissolved oxygen (% saturation) with season and depth at the Kingston site (CRK 1.6).

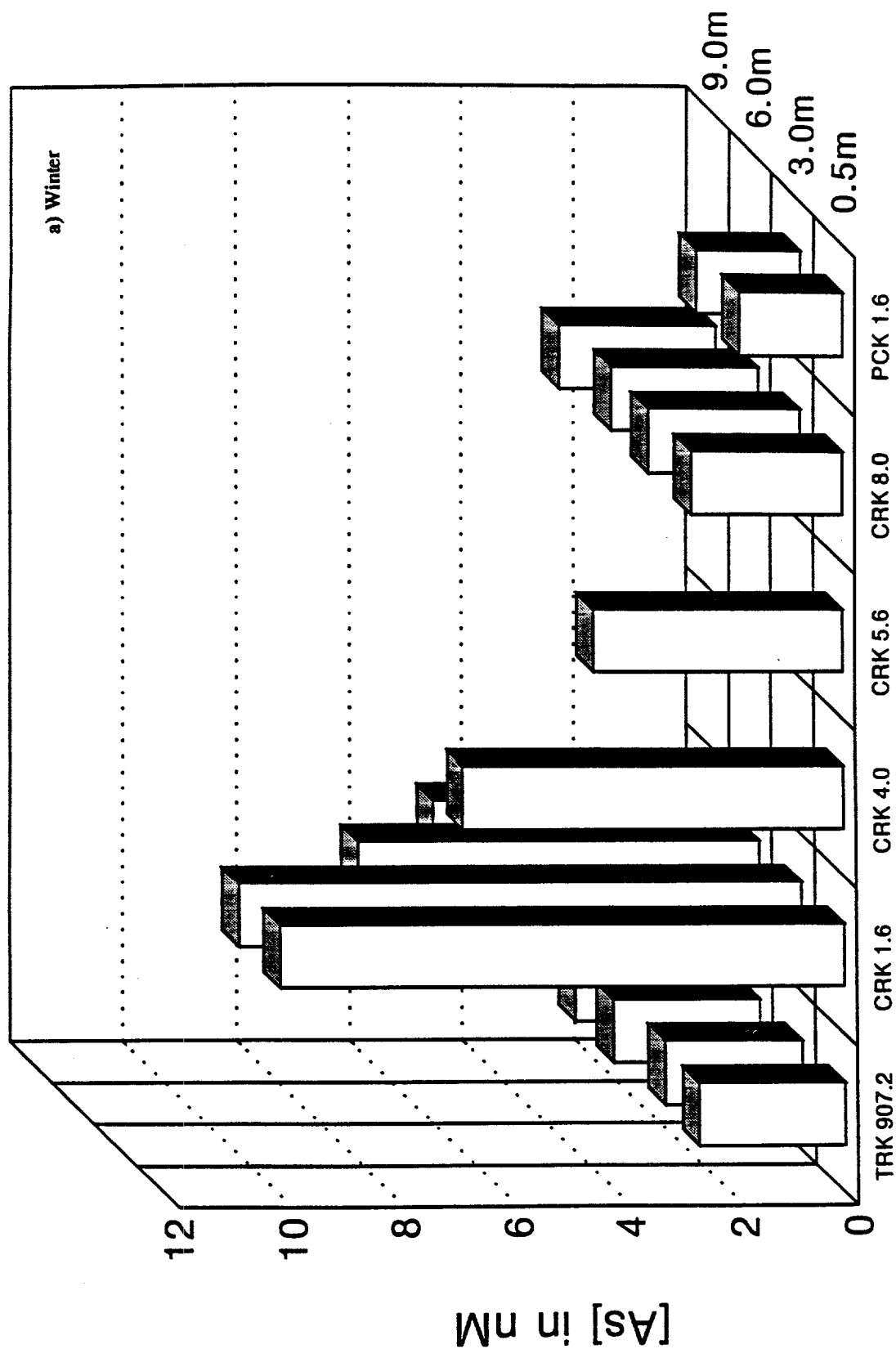


Fig. 7(a). Bar chart of total dissolved inorganic arsenic (nM) for several sites and depths for surface water in the Kingston (TRK 907.2, CRK 1.6, CRK 4.0, CRK 5.6, and CRK 8.0) and Poplar Creek (CRM 18.4, PCK 0.25, PCK 1.6) areas. Winter.

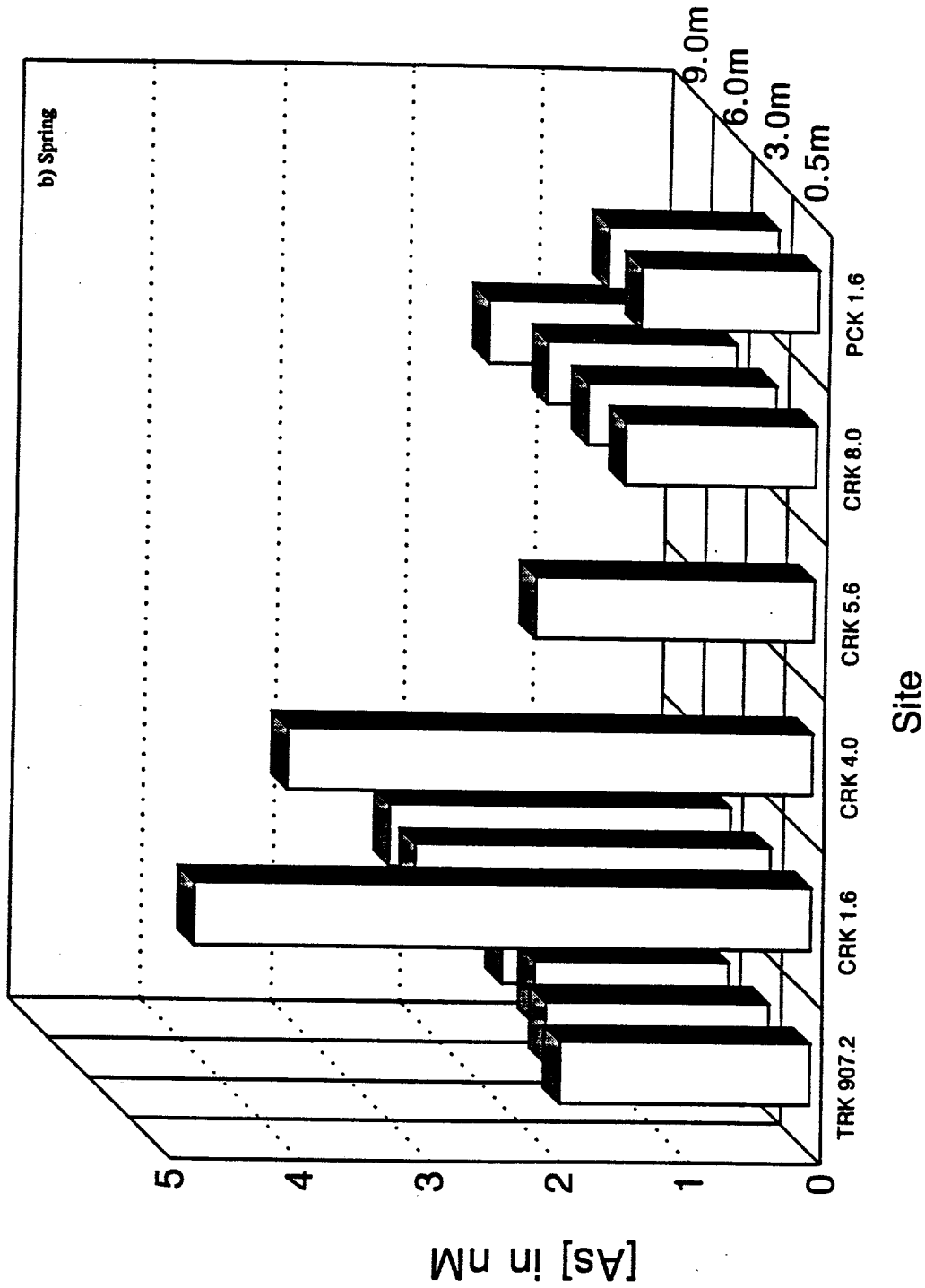


Fig. 7(b). Bar chart of total dissolved inorganic arsenic (nM) for several sites and depths for surface water in the Kingston (TRK 907.2, CRK 1.6, CRK 4.0, CRK 5.6, and CRK 8.0) and Poplar Creek (CRM 18.4, PCK 0.25, PCK 1.6) areas. Spring.

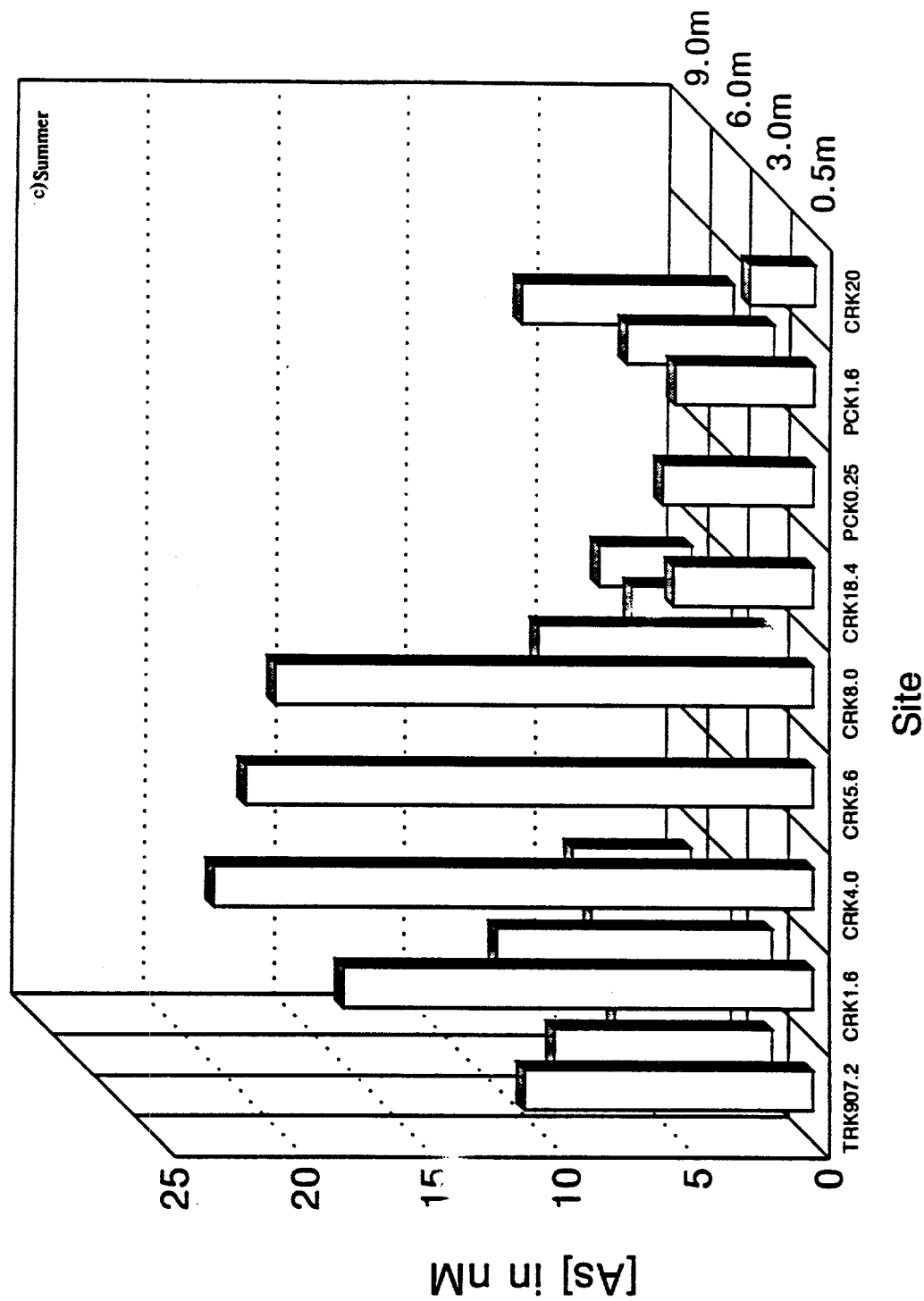


Fig. 7(c). Bar chart of total dissolved inorganic arsenic (nM) for several sites and depths for surface water in the Kingston (TRK 907.2, CRK 1.6, CRK 4.0, CRK 5.6, and CRK 8.0) and Poplar Creek (CRK 18.4, PCK 0.25, PCK 1.6) areas. Summer.

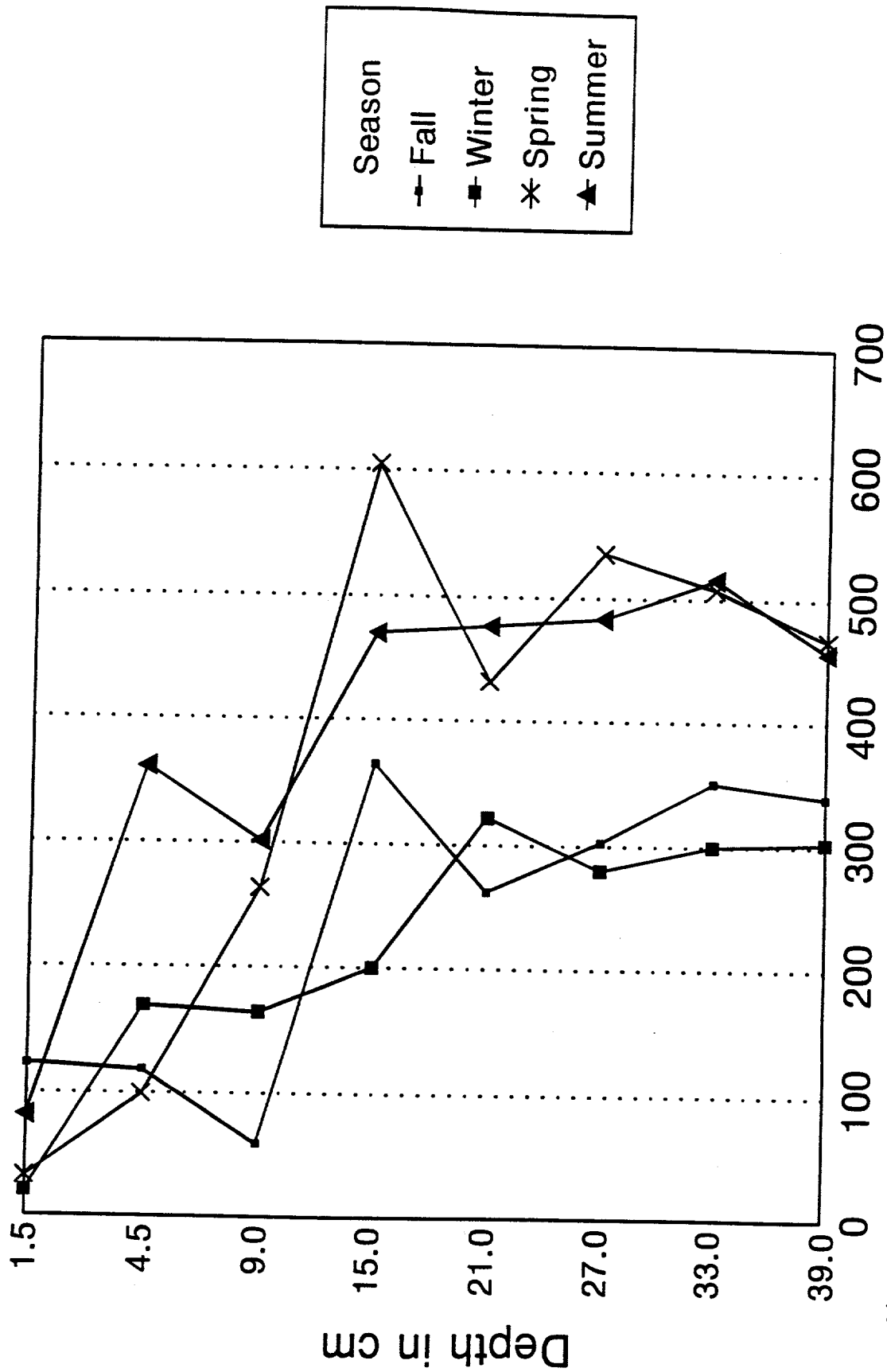


Fig. 8. Profile of total dissolved inorganic arsenic (nM) in pore water by depth in the sediment for each season in the Kingston area (CRK 1.6).

Table 8. Mean surface sediment (<5 cm) inorganic As, As(III), and As(V) concentrations (nM) for pore water for each season from Kingston^a

Season	N	Inorganic As	As(III)	As(V)
Winter	2	94	10	84
Spring	2	65	8	57
Summer	6	221	103	118
Fall	2	120	3	117

^aF statistic values for concentrations for each season are not significantly different at a $p < 0.05$.

Table 9. Mean inorganic As, As(III), and As(V) concentrations (nM) for pore water for each season in Kingston^a

Season	N	Inorganic As (Group)	As(III) (Group)	As(V) (Group)
Winter	8	219 (B)	52 (A)	167 (B)
Spring	9	386 (A)	100 (A)	286 (A)
Summer	36	419 (A)	128 (A)	291 (A)
Fall	8	239 (B)	89 (A)	150 (B)

^aDifferent grouping letters (A, B) indicate significantly different F statistic values at a $p < 0.05$.

Table 10. The mean inorganic As, AsIII, and AsV concentrations (nM) of each source by site*

Site	N	Mean Inorganic As (Group)	Mean AsIII (Group)	Mean AsV (Group)
Kingston				
TRK 907.2	16	3.26 (C)	0.26 (A)	3.00 (C)
CRK 1.6	45	7.15 (ABC)	0.62 (A)	6.53 (ABC)
CRK 4.0	3	11.27 (A)	0.54 (A)	10.73 (A)
CRK 5.6	3	9.45 (AB)	0.60 (A)	8.85 (AB)
CRK 8.0	16	3.90 (BC)	0.27 (A)	3.63 (AB)
Lower McCoy Branch				
CRK 60.5	21	2.74 (C)	0.17 (B)	2.57 (C)
MBK 0.3	65	6.02 (B)	0.63 (B)	5.39 (B)
MBK 0.5	11	14.0 (A)	1.63 (A)	12.37 (A)
Bull Run Steam Plant				
CRK 66.7	8	3.15 (A)	0.42 (A)	2.73 (A)
CRK 73.6	2	3.86 (A)	0.58 (A)	3.28 (A)
CRK 78.4	1	2.00 (A)	0.01 (A)	1.99 (A)
CRK 80.0	3	1.91 (A)	0.03 (A)	1.88 (A)
Upper McCoy Branch				
MBK 0.7	13	39.16 (A)	3.49 (A)	35.67 (A)
MBK 0.9	6	71.10 (A)	3.39 (A)	67.71 (A)
Rogers Quarry				
MBK 1.6	58	222.00 (A)	6.44 (A)	215.56 (A)
MBK 1.8	19	170.00 (B)	1.33 (A)	168.67 (B)
MBK 2.0	48	35.60 (C)	0.57 (A)	35.03 (C)

*Different grouping letters (A, B, C) indicate significantly different F statistic values at a $p < 0.05$. Groupings are relative to each source.

Table 11. The mean inorganic As, AsIII, and AsV concentrations (nM) from each source site by season^a

Season	Site	n	Mean inorganic As (Group)	Mean AsIII (Group)	Mean AsV (Group)
Kingston					
Winter	TRK 907.2	6	2.48 (A)	0.09 (A)	2.39 (A)
	CRK 1.6	10	7.31 (A)	0.05 (BC)	7.26 (A)
	CRK 4.0	1	6.75 (A)	0.07 (AB)	6.68 (A)
	CRK 5.6	1	4.40 (A)	0.04 (BC)	4.36 (A)
	CRK 8.0	5	2.70 (A)	0.02 (C)	2.68 (A)
Spring	TRK 907.2	6	1.57 (A)	0.05 (A)	1.52 (A)
	CRK 1.6	10	2.98 (A)	0.06 (A)	2.92 (A)
	CRK 4.0	1	4.06 (A)	0.16 (A)	3.90 (A)
	CRK 5.6	1	2.14 (A)	0.03 (A)	2.11 (A)
	CRK 8.0	6	1.49 (A)	0.03 (A)	1.46 (A)
Summer	TRK 907.2	6	5.74 (B)	0.63 (A)	5.11 (B)
	CRK 1.6	20	8.57 (B)	1.05 (A)	7.52 (B)
	CRK 4.0	1	23.00 (A)	1.40 (A)	21.60 (A)
	CRK 5.6	1	21.80 (A)	1.73 (A)	20.07 (A)
	CRK 8.0	5	7.99 (B)	0.79 (A)	7.20 (B)
Lower McCoy Branch					
Winter	CRK 60.5	6	3.41 (B)	0.03 (A)	3.38 (B)
	MBK 0.3	23	4.94 (B)	0.25 (A)	4.69 (B)
	MBK 0.5	5	8.36 (A)	0.11 (A)	8.25 (A)
Spring	CRK 60.5	4	2.57 (B)	0.24 (A)	2.33 (B)
	MBK 0.3	12	3.81 (B)	0.26 (A)	3.55 (B)
	MBK 0.5	1	24.00 (A)	0.18 (A)	23.82 (A)
Summer	CRK 60.5	11	2.43 (C)	0.22 (C)	2.21 (C)
	MBK 0.3	25	8.59 (B)	1.17 (B)	7.42 (B)
	MBK 0.5	5	17.65 (A)	3.43 (A)	14.22 (A)

^aDifferent grouping letters (A, B, C) indicate significantly different F statistics at a $p < 0.05$. Groupings are relative to each source and each season.

Table 12. The mean inorganic As, AsIII, and AsV concentrations (nM) from each Kingston, Poplar Creek, and lower McCoy Branch depth by season^a

Season	Depth (m)	N	Mean inorganic As (Group)	Mean AsIII (Group)	Mean AsV (Group)
Kingston					
Winter	0.5	4	6.32 (A)	0.08 (B)	6.24 (A)
	3.0	4	6.27 (A)	0.05 (B)	6.22 (A)
	6.0	4	4.86 (A)	0.05 (B)	4.81 (A)
	9.0	4	3.84 (A)	0.05 (B)	3.79 (A)
	12.0	1	2.25 (A)	0.12 (A)	2.13 (A)
Spring	0.5	4	3.22 (A)	0.05 (A)	3.17 (A)
	3.0	4	2.49 (A)	0.08 (A)	2.41 (A)
	6.0	4	2.05 (A)	0.05 (A)	2.00 (A)
	9.0	5	1.97 (A)	0.03 (A)	1.94 (A)
Summer	0.5	6	17.26 (A)	2.26 (A)	15.00 (AB)
	3.0	6	9.87 (B)	1.23 (AB)	8.64 (BC)
	6.0	6	4.92 (B)	0.55 (AB)	4.37 (C)
	9.0	6	4.14 (B)	0.41 (B)	3.73 (C)
	12.0	5	4.24 (B)	0.39 (B)	3.85 (C)
Poplar Creek					
Summer	0.5	3	5.34 (B)	0.36 (B)	4.98 (B)
	1.0	2	5.42 (B)	0.14 (B)	5.28 (B)
	2.0	3	5.82 (B)	0.30 (B)	5.52 (B)
	3.0	2	5.62 (B)	0.18 (B)	5.44 (B)
	4.0	3	5.78 (B)	0.43 (B)	5.35 (B)
	4.9	1	9.27 (A)	1.25 (A)	8.02 (A)
	5.0	1	8.10 (A)	0 (B)	8.10 (A)
Lower McCoy Branch					
Summer	0.0	2	14.75 (ABC)	1.93 (BC)	12.82 (ABC)
	0.5	8	7.04 (ABCD)	0.92 (BC)	6.12 (ABCD)
	1.0	2	8.64 (ABCD)	0.81 (C)	7.83 (ABCD)
	2.0	5	6.77 (BCD)	0.88 (BC)	5.89 (ABCD)
	3.0	6	5.29 (BCD)	0.77 (C)	4.52 (BCD)
	4.0	3	17.96 (A)	4.20 (A)	13.76 (A)
	5.0	3	15.67 (AB)	2.57 (B)	13.10 (AB)
	6.0	4	3.99 (CD)	0.46 (C)	3.53 (CD)

^aDifferent grouping letters (A, B, C, D) indicate significantly different F statistic values at a $p < 0.05$. Groupings are relative to each source.

Table 13. The mean inorganic As, As(III), and As(V) concentrations (nM) in water from sources in Watts Bar Reservoir and sites in Melton Hill Reservoir^a

Watts Bar Reservoir				
Source	N	Mean Inorganic As (Group)	Mean As(III) (Group)	Mean As(V) (Group)
Lower Watts Bar Reservoir	113	3.50 (B)	0.22 (B)	3.28 (B)
Kingston	85	5.94 (A)	0.47 (A)	5.47 (A)
Poplar Creek	34	4.16 (B)	0.27 (B)	3.89 (B)
Melton Hill Reservoir				
CRK 60.5	21	2.74 (C)	0.17 (A)	2.57 (C)
MBK 0.3	65	6.02 (CB)	0.63 (A)	5.39 (CB)
MBK 0.5	11	14.00 (CB)	1.62 (A)	12.38 (CB)
MBK 0.7	13	39.16 (CB)	3.49 (A)	35.67 (CB)
MBK 0.9	6	71.10 (B)	3.39 (A)	67.71 (B)
MBK 1.6	58	222.02 (A)	6.44 (A)	215.58 (A)
MBK 1.8	19	170.05 (A)	1.33 (A)	168.72 (A)
MBK 2.0	48	35.63 (CB)	0.57 (A)	35.06 (CB)
CRK 66.7	8	3.15 (C)	0.42 (A)	2.73 (C)
CRK 73.6	2	3.86 (C)	0.58 (A)	3.28 (C)
CRK 78.4	1	2.00 (C)	0.01 (A)	1.99 (C)
CRK 80.0	3	1.91 (C)	0.27 (A)	1.64 (C)

^aDifferent group letters (A, B, C) indicate significantly different F statistic values at a $p < 0.05$. Groupings are relative to each source.

Table 14. The mean inorganic As, AsIII, and AsV concentrations (nM) from each source during summer^a

Source	N	Mean Inorganic As (Group)	Mean AsIII (Group)	Mean AsV (Group)
Lower Watts Bar Reservoir	49	4.41 (C)	0.36 (B)	4.05 (C)
Kingston	33	8.80 (A)	0.96 (A)	7.84 (A)
Poplar Creek	18	5.78 (B)	0.31 (B)	5.47 (B)

^aDifferent grouping letters (A, B, C) indicate significantly different F statistic values at a $p < 0.05$.

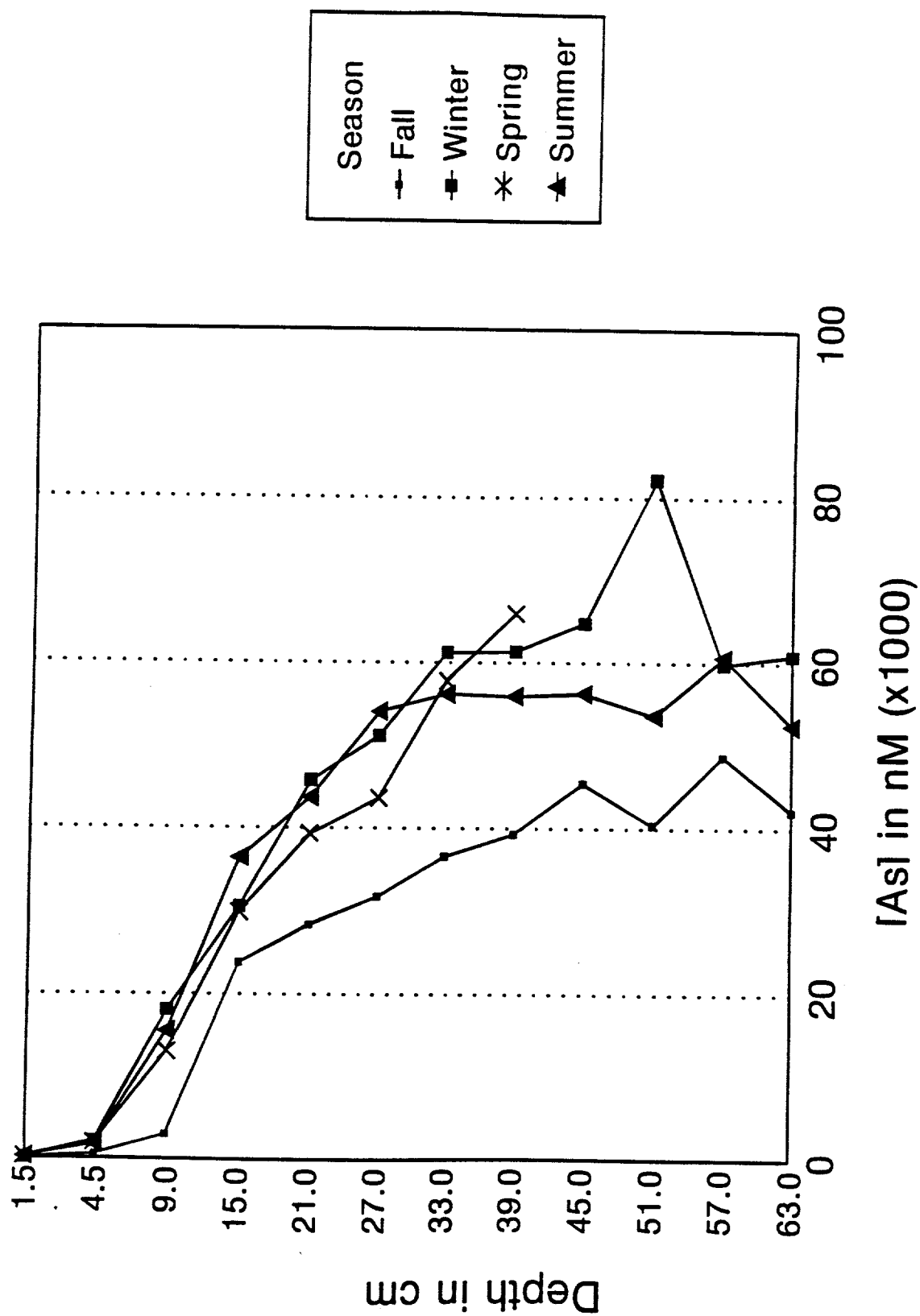


Fig. 9. Profile of total dissolved inorganic arsenic (nM) in pore water by depth in the sediment for each season in Poplar Creek (PCK 1.6).

Table 15. Mean inorganic As, As(III), and As(V) concentrations (nM) for pore water in Poplar Creek for each season^a

Season	N	Inorganic As (Group)	As(III) (Group)	As(V) (Group)
Winter	14	47,289 (A)	36,506 (A)	10,782 (A)
Spring	8	31,425 (C)	25,538 (BC)	5,887 (A)
Summer	37	40,771 (B)	33,195 (AB)	7,576 (A)
Fall	12	28,260 (C)	23,303 (C)	4,957 (A)

^aDifferent grouping letters (A, B, C) indicate significantly different F statistic values at a $p < 0.05$.

Table 16. Mean arsenic, iron, and manganese K_D for each season in sediment from Poplar Creek^a

Season	N	As K_D	N	Fe K_D	N	Mn K_D
Spring	2	35 (A)	2	47,155 (A)	2	487 (A)
Summer	34	231 (A)	26	17,686 (A)	26	173 (B)
Fall	11	617 (A)	10	192,500 (A)	10	165 (B)

^aDifferent grouping letters (A, B) indicate significantly different F statistic values at a $p < 0.05$.

Table 17. Mean arsenic, iron, and manganese K_D for each sediment depth in Poplar Creek^a

Depth (cm)	N	As K_D	N	Fe K_D	N	Mn K_D
1.5	5	1750 (A)	4	43,722 (A)	4	400 (A)
4.5	4	815 (B)	4	54,017 (A)	4	174 (A)
9.0	5	100 (B)	4	24,536 (A)	4	145 (A)
15.0	3	44 (B)	4	51,089 (A)	4	163 (A)
21.0	3	152 (B)	4	82,059 (A)	4	141 (A)
27.0	4	57 (B)	4	74,737 (A)	4	167 (A)
33.0	3	38 (B)	4	273,684 (A)	4	162 (A)

^aDifferent group letters (A, B) indicate significantly different F statistic values at a $p < 0.05$.

Table 18. Mean inorganic As, As(III), and As(V) concentrations (nM) for sediment pore water by depth in Poplar Creek^a

Depth (cm)	N	Inorganic As	As(III)	As(V)
1.5	6	233 (D)	20 (C)	213 (A)
4.5	6	1,672 (D)	470 (CB)	1,202 (A)
9.0	6	13,410 (D)	8,487 (CB)	4,923 (A)
15.0	6	32,090 (C)	24,067 (BA)	8,023 (A)
21.0	5	40,642 (CAB)	34,060 (A)	6,582 (A)
27.0	6	48,042 (CAB)	36,883 (A)	11,158 (A)
33.0	5	53,880 (AB)	46,522 (A)	7,358 (A)

^aDifferent grouping letters indicate significantly different F statistic values at a $p < 0.05$.

Table 19. Mean surface sediment pore water (<5 cm) inorganic As, As(III), and As(V) concentrations (nM) and statistical grouping values for each source^a

Summer				
Source	N	Inorganic As (Group)	As(III) (Group)	As(V) (Group)
Lower Watts Bar Reservoir	12	170.1 (C)	49.3 (B)	120.8 (C)
Kingston	12	157.4 (C)	55.4 (B)	102.0 (C)
Poplar Creek	12	952.4 (B)	254.1 (B)	698.3 (B)
Lower McCoy Branch	26	403.1 (BC)	78.1 (B)	325.0 (BC)
Upper McCoy Branch	8	2106.3 (A)	930.2 (A)	1176.1 (A)

^aDifferent group letters (A, B, C) indicate significantly different F statistic values at a $p < 0.05$.

Table 20. Mean surface sediment pore water (<5 cm) inorganic As, As(III), and As(V) concentrations (nM) for each season from Poplar Creek^a

Season	N	Inorganic As	As(III)	As(V)
Winter	2	1170	695	475
Spring	2	1150	302	848
Summer	6	1011	140	871
Fall	2	360	50	310

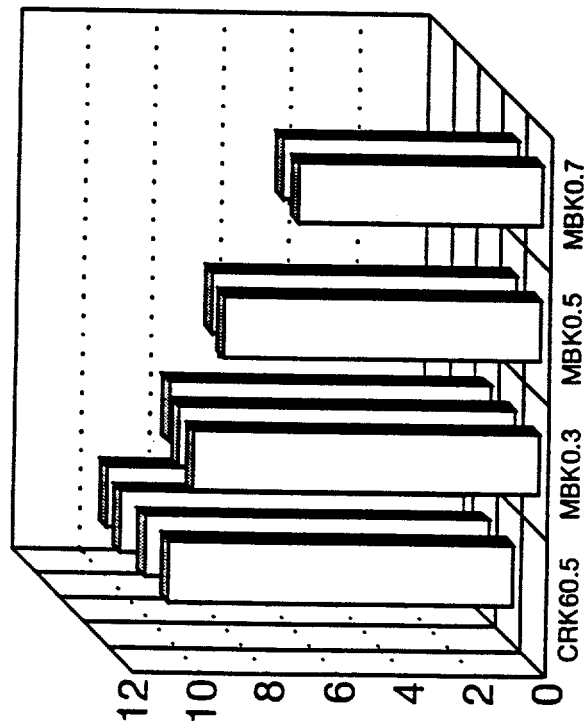
^aF statistic values for concentrations for each season are not significantly different at a $p < 0.05$.

Table 21. Mean surface sediment pore water (<5 cm) inorganic As, As(III), and As(V) concentrations (nM) and statistical grouping values for each source in summer and winter^a

Source	Summer				Winter			
	N	Inorganic As (Group)	As(III) (Group)	As(V) (Group)	N	Inorganic As (Group)	As(III) (Group)	As(V) (Group)
Lower Watts Bar Reservoir	6	276 (B)	79 (B)	197 (BC)	2	9.3 (B)	0.2 (B)	9.1 (B)
Kingston	6	221 (B)	103 (B)	118 (C)	2	94 (AB)	10 (AB)	84 (B)
Poplar Creek	6	1011 (B)	140 (B)	871 (B)	2	1170 (A)	695 (A)	475 (AB)
Lower McCoy Branch	12	696 (B)	154 (B)	542 (BC)	10	93 (B)	5 (B)	88 (AB)
Upper McCoy Branch	4	3370 (A)	1558 (A)	1812 (A)	4	842 (AB)	301 (AB)	540 (A)

^aDifferent group letters (A, B, C) indicate significantly different F statistic values at a p<0.05.

Temperature (degrees C)



Dissolved Oxygen (% saturation)

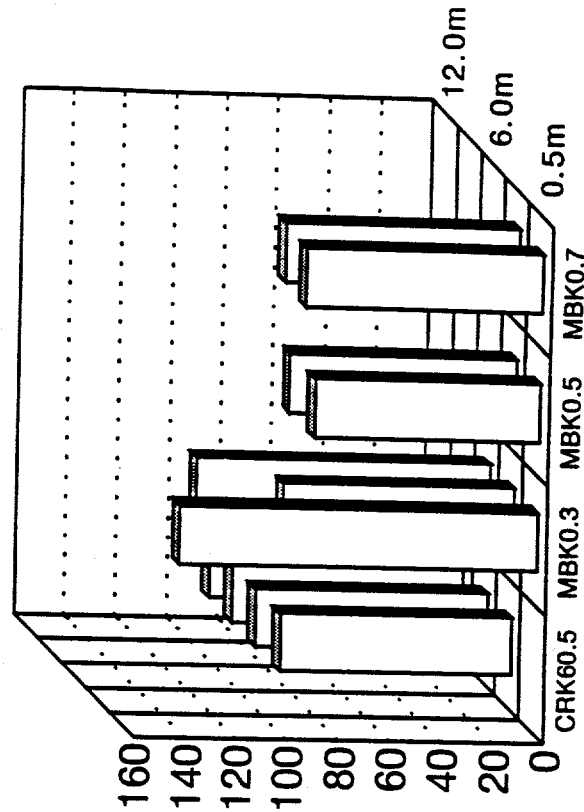
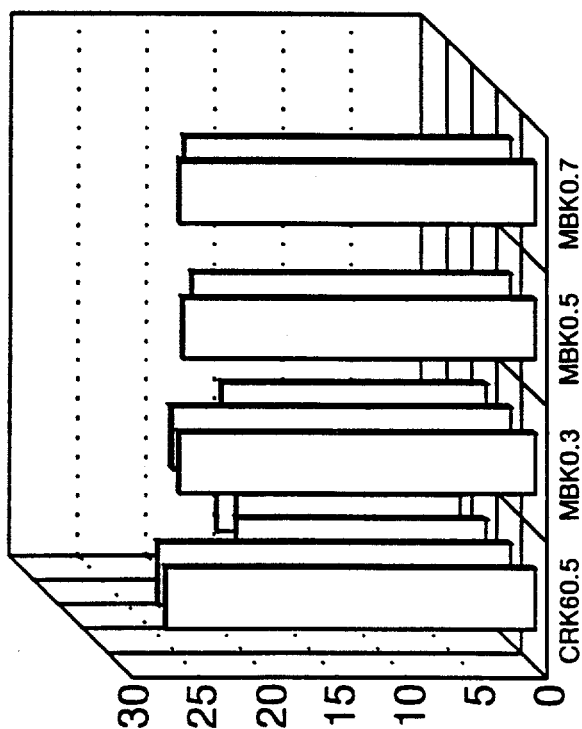


Fig. 10(a). Bar charts of water temperature (degrees C) and dissolved oxygen (% saturation) with season and depth in lower McCoy Branch Embayment (CRK 60.5, MBK 0.3, MBK 0.5) and upper McCoy Branch Embayment (MBK 0.7, MBK 0.85). Winter.

Temperature (degrees C)



Dissolved Oxygen (% saturation)

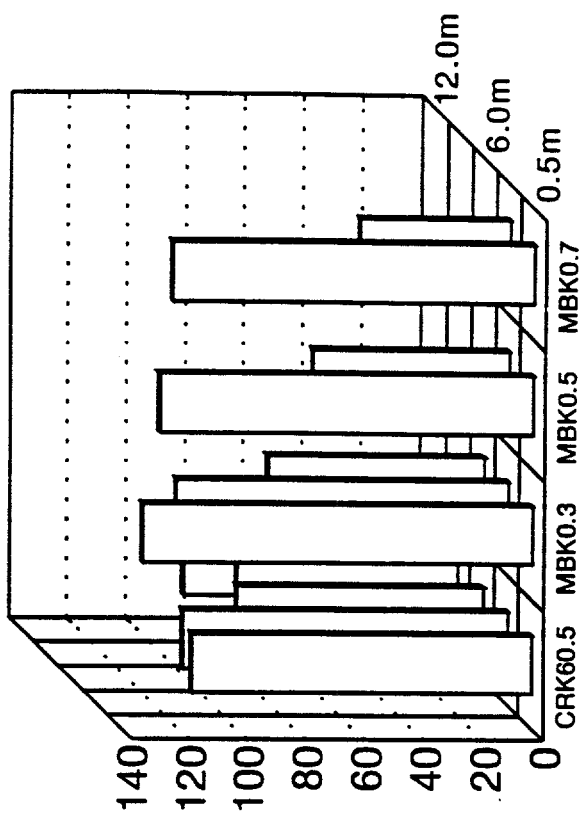


Fig. 10(b). Bar charts of water temperature (degrees C) and dissolved oxygen (% saturation) with season and depth in lower McCoy Branch Embayment (CRK 60.5, MBK 0.3, MBK 0.5) and upper McCoy Branch Embayment (MBK 0.7, MBK 0.85). Summer.

Temperature (degrees C) Dissolved Oxygen (% saturation)

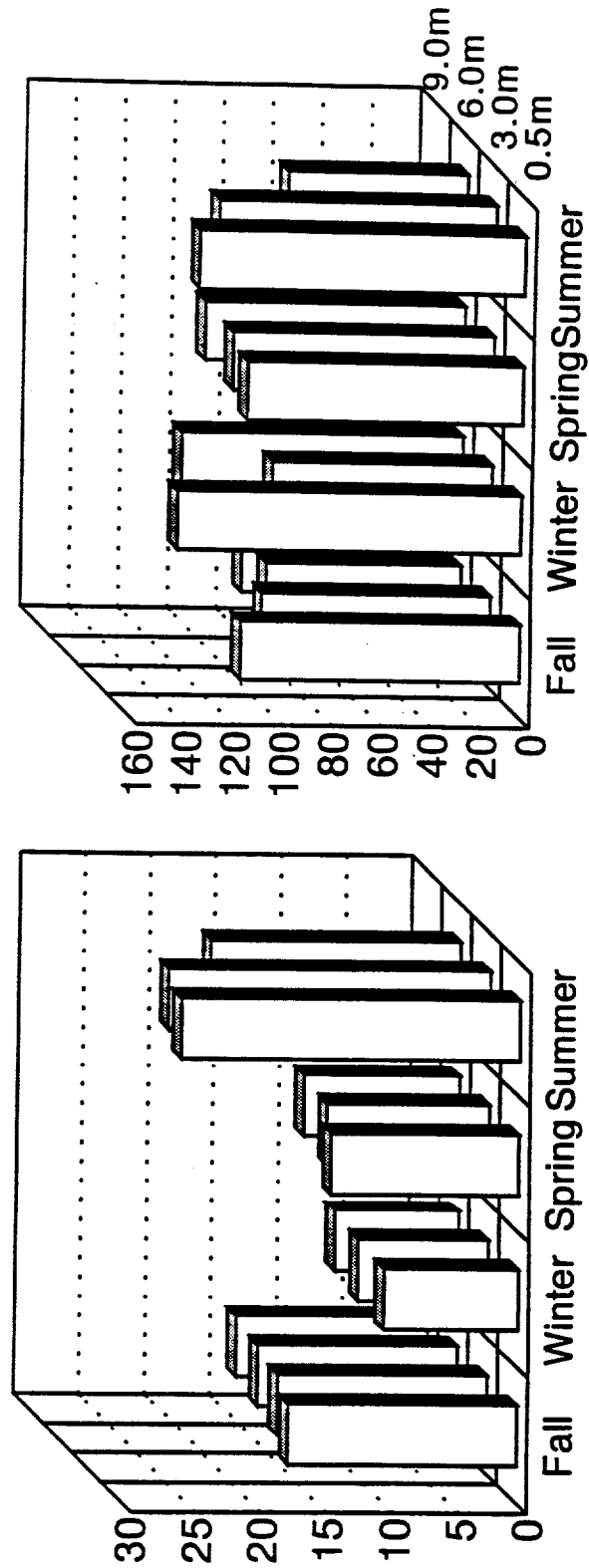


Fig. 11. Bar charts of water temperature (degrees C) and dissolved oxygen (% saturation) with season and depth in lower McCoy Branch Embayment (MBK 0.3).



Fig. 12(a). Bar chart of total dissolved inorganic arsenic (nM) for several sites and depths for surface water in the lower McCoy Branch Embayment (CRK 60.5, MBK 0.3, MBK 0.5) and upper McCoy Branch Embayment (MBK 0.7, MBK 0.85) areas. Winter.

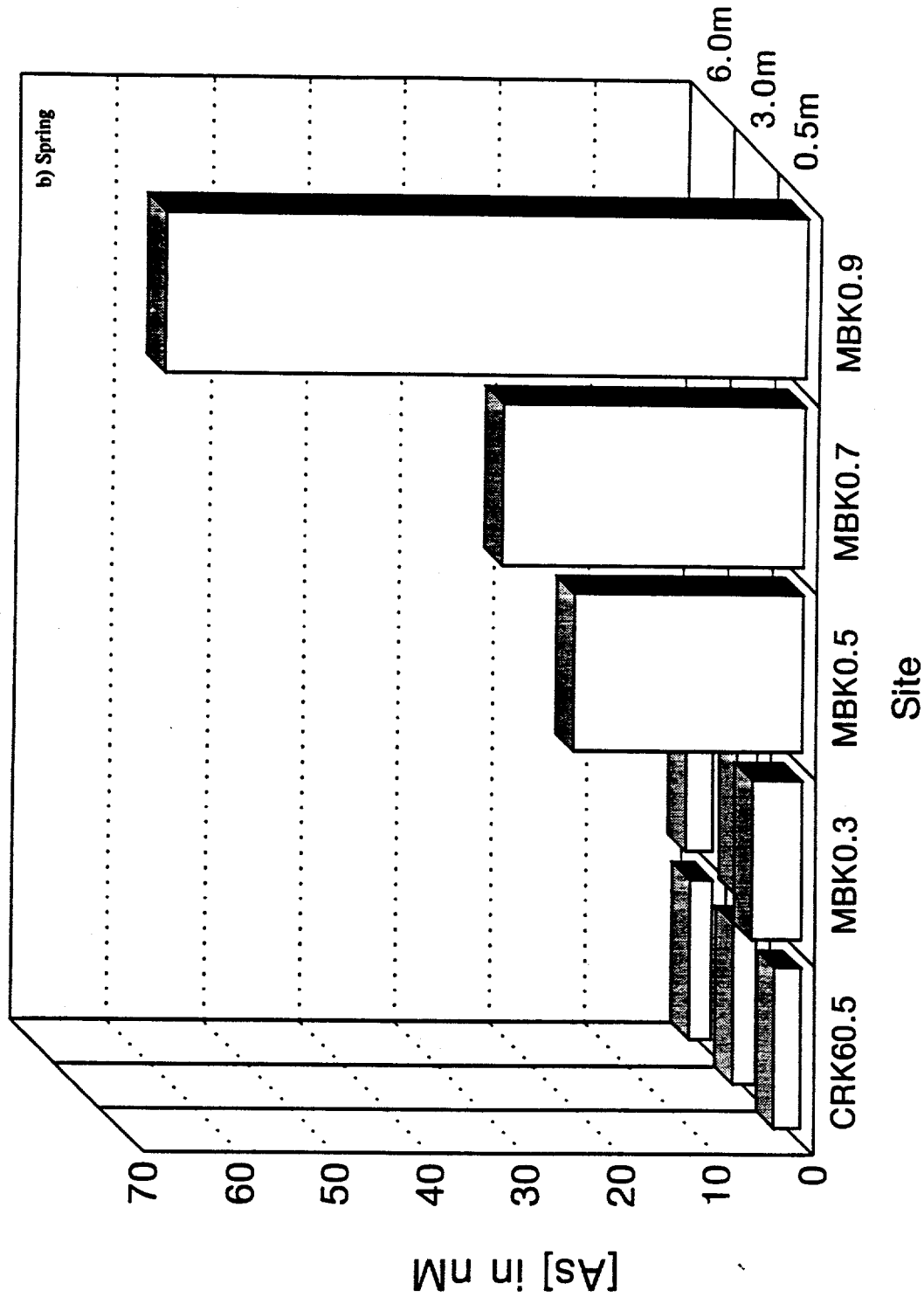


Fig. 12(b). Bar chart of total dissolved inorganic arsenic (nM) for several sites and depths for surface water in the lower McCoy Branch Embayment (CRK 60.5, MBK 0.3, MBK 0.5) and upper McCoy Branch Embayment (MBK 0.7, MBK 0.85) areas. Spring.

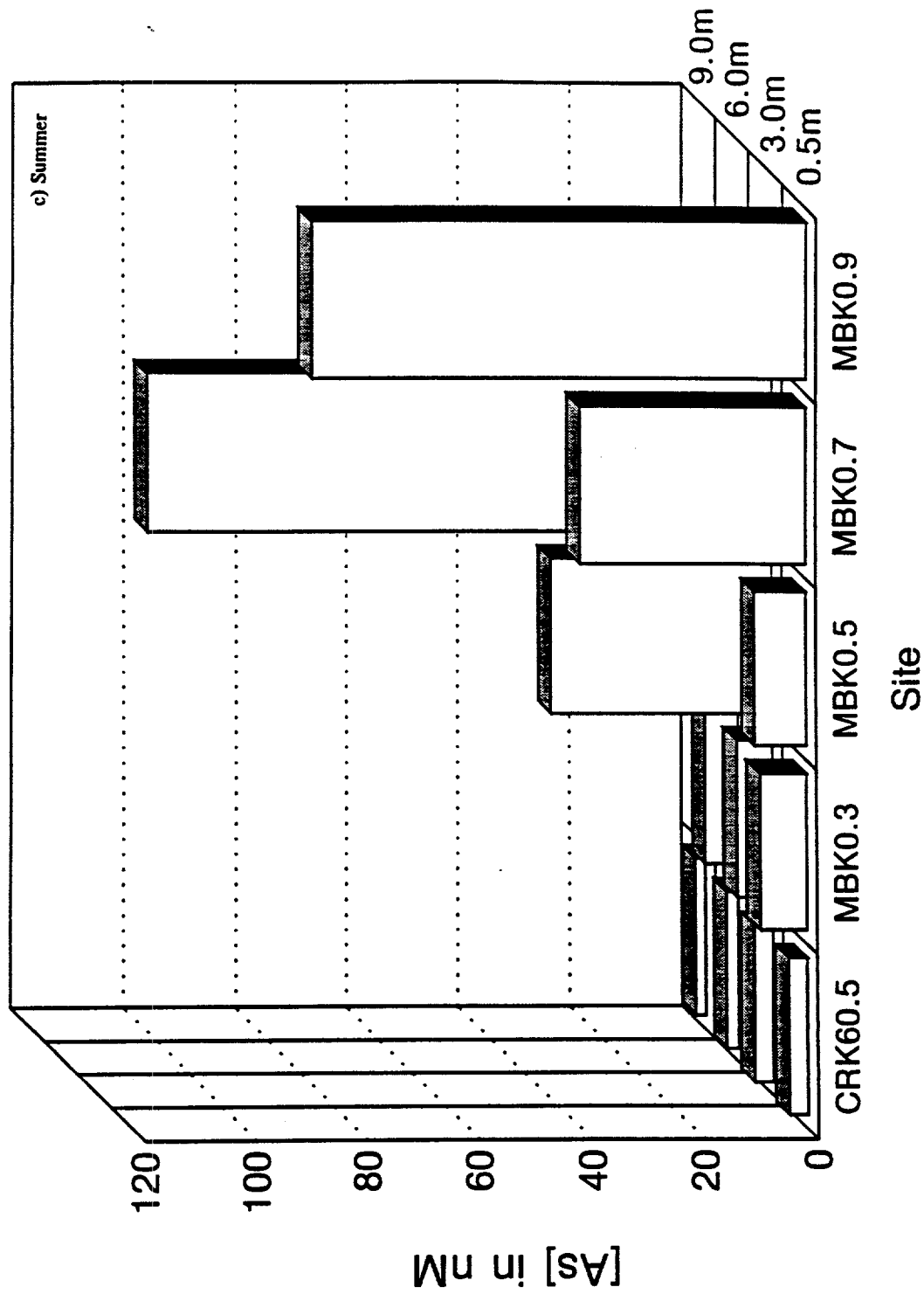


Fig. 12(c). Bar chart of total dissolved inorganic arsenic (nM) for several sites and depths for surface water in the lower McCoy Branch Embayment (CRK 60.5, MBK 0.3, MBK 0.5) and upper McCoy Branch Embayment (MBK 0.7, MBK 0.85) areas. Summer.

Table 22. Mean inorganic As, As(III), and As(V) concentrations (nM) for pore water by site in lower McCoy Branch^a

Site	N	Inorganic As (Group)	As(III) (Group)	As(V) (Group)
CRK 60.5	16	150 (B)	30 (C)	120 (B)
MBK 0.3	88	547 (A)	164 (B)	383 (A)
MBK 0.5	10	748 (A)	338 (A)	410 (A)

^aDifferent group letters (A, B) indicate significantly different F statistic values at a $p > 0.05$.

Table 23. Mean inorganic As, As(III), and As(V) concentrations (nM) for pore water by depth in the sediment from lower McCoy Branch^a

Depth (cm)	N	Inorganic As	As(III)	As(V)
1.5	13	264	22	242
4.5	13	542	134	408
9.0	13	779	261	518
15.0	13	547	198	349
21.0	13	409	127	281
27.0	11	443	144	299
33.0	11	561	182	379

^aF statistic values for sediment depths are not significantly different at a $p < 0.05$.

Table 24. Mean inorganic As, As(III), and As(V) concentrations (nM) for pore water in lower McCoy Branch for each season

Season	N	Inorganic As	As(III)	As(V)
Winter	44	368	96	272
Spring	8	446	152	294
Summer	50	627	224	403
Fall	12	576	140	436

^aF statistic values for seasons are not significantly different at a $p < 0.05$.

Table 25. Mean inorganic As, As(III), and As(V) concentrations (nM) for pore water by site for winter and summer in lower McCoy Branch^a

Site	N	Winter			N	Summer		
		Inorganic As (Group)	As(III) (Group)	As(V) (Group)		Inorganic As (Group)	As(III) (Group)	As(V) (Group)
CRK 60.5	8	113 (B)	24 (B)	89 (B)	8	188 (B)	37 (C)	149 (B)
MBK 0.3	31	416 (A)	121 (A)	340 (A)	37	632 (B)	211 (B)	421 (AB)
MBK 0.5	5	202 (B)	62 (A)	140 (B)	5	1294 (A)	614 (A)	679 (A)

^aDifferent group letters (A, B) indicate significantly different F statistic values at a $p < 0.05$.

Table 26. Mean surface sediment (<5 cm) inorganic As, As(III), and As(V) concentrations (nM) and statistical grouping values for each site from lower McCoy Branch^a

Site	N	Inorganic As (Group)	As(III) (Group)	As(V) (Group)
CRK 60.5	4	86 (A)	1.5 (B)	84.5 (A)
MBK 0.3	18	421 (A)	48 (B)	373 (A)
MBK 0.5	4	638 (A)	286 (A)	352 (A)

^aDifferent group letters (A, B) indicate significantly different F statistic values at a $p < 0.05$.

Table 27. Mean arsenic, iron, and manganese K_D for each sediment depth in lower McCoy Branch^a

Depth (cm)	N	As K_D	N	Fe K_D	N	Mn K_D
1.5	10	5541	7	71,254	7	2767
4.5	10	1179	8	48,733	8	755
9.0	10	749	7	9,677	8	1378
15.0	10	461	8	122,027	8	889
21.0	9	731	7	10,837	7	625
27.0	8	826	6	9,388	6	600
33.0	8	645	6	4,258	6	401

^aF statistic values for each depth are not significantly different at a $p < 0.05$

Table 28. Mean arsenic, iron, and manganese sediment to pore water K_D for each season from lower McCoy Branch and upper McCoy Branch^a

Season	Lower McCoy Branch				Upper McCoy Branch							
	N	As K _D (Group)	N	Fe K _D (Group)	N	Mn K _D (Group)	N	As K _D (Group)	N	Fe K _D (Group)	N	Mn K _D (Group)
Winter	32	2405 (A)	30	23,103 (B)	30	1090 (A)	19	585 (A)	19	25,793 (A)	19	3113 (A)
Summer	40	366 (A)	22	15,705 (B)	22	584 (A)	21	194 (B)	19	14,389 (A)	19	285 (A)
Fall	11	1469 (A)	8	138,100 (A)	10	1906 (A)	N/A	N/A	N/A	N/A	N/A	N/A

Different group letters (A, B) indicate significantly different F statistic values at a p<0.05.

^aDifferent group letters (A, B) indicate significantly different F statistic values at a $p < 0.05$.

Table 29. The mean arsenic, iron, and manganese K_D for each sediment depth in lower McCoy Branch in winter and summer^a

Depth (cm)	Winter				Summer							
	N	As K _D (Group)	N	Fe K _D (Group)	N	Mn K _D (Group)	N	As K _D (Group)	N	Fe K _D (Group)	N	Mn K _D (Group)
1.5	4	10,692 (A)	4	76,705 (A)	4	4253 (A)	5	1092 (A)	2	52,229 (A)	2	1078 (A)
4.5	4	2,542 (A)	4	57,569 (AB)	4	880 (A)	5	217 (A)	3	42,085 (A)	3	772 (A)
9	4	1,244 (A)	4	8,038 (B)	4	572 (A)	5	176 (A)	3	11,861 (A)	3	579 (A)
15	4	781 (A)	4	11,167 (AB)	4	895 (A)	5	252 (A)	3	10,516 (A)	3	677 (A)
21	4	1,252 (A)	3	8,141 (B)	3	593 (A)	5	314 (A)	3	6,035 (A)	3	533 (A)
27	4	1,024 (A)	3	6,957 (B)	3	539 (A)	4	268 (A)	2	6,064 (A)	3	493 (A)
33	4	762 (A)	3	4,020 (B)	3	411 (A)	4	502 (A)	2	3,966 (A)	2	420 (A)

Different grouping letters (A, B) indicate significantly different E statistics values at P < 0.05

^aDifferent grouping letters (A, B) indicate significantly different F statistic values at a $p < 0.05$.

Table 30. Mean surface sediment (<5 cm) inorganic As, As(III), and As(V) concentrations (nM) for each season from Lower McCoy Branch.^a

Season	N	Inorganic As	As(III)	As(V)
Winter	10	93	5	88
Spring	2	183	17	166
Summer	12	696	154	542
Fall	2	411	46	365

^aF statistic values for concentrations for each season are not significantly different at a $p < 0.05$.

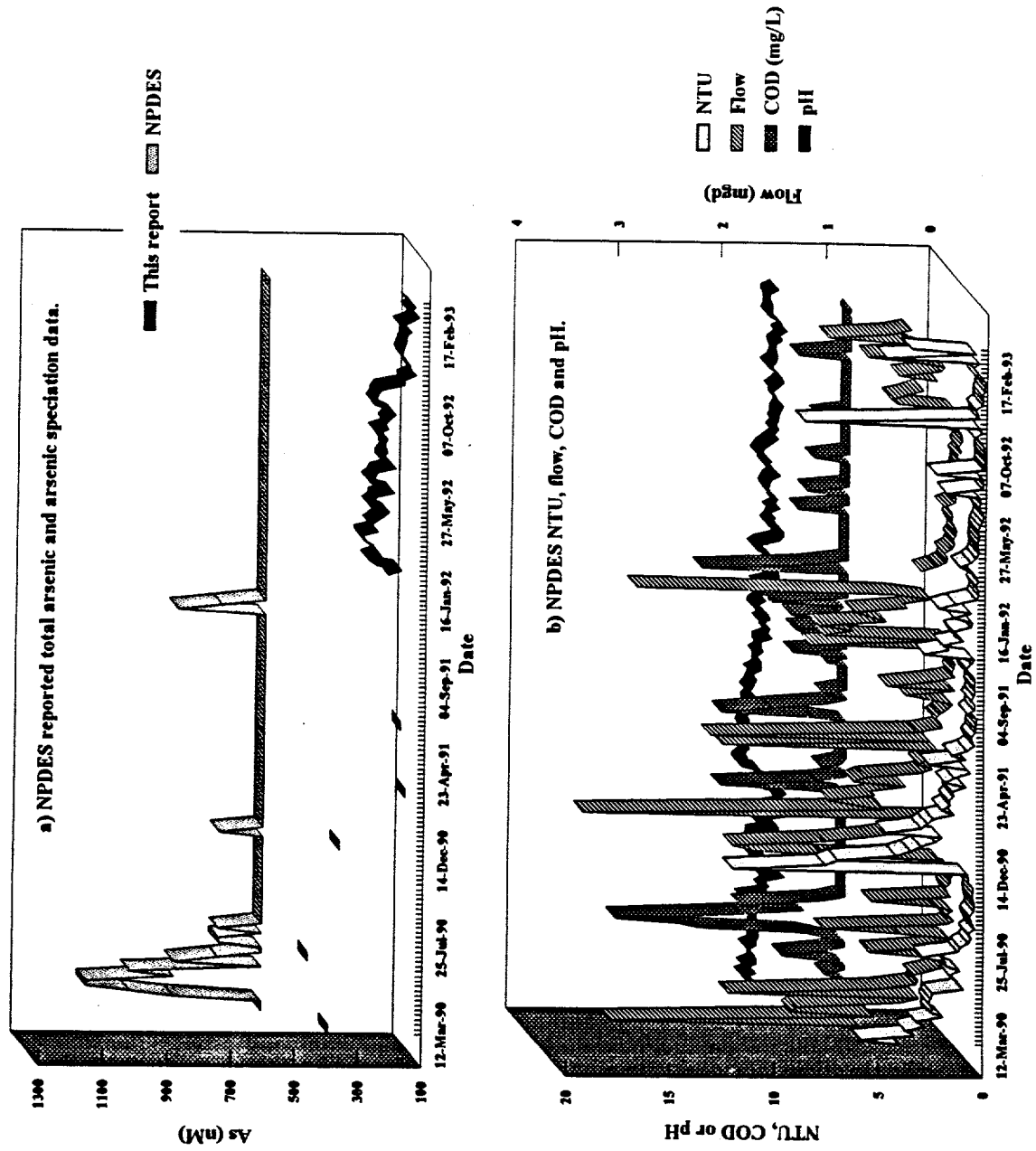


Fig. 13. Line plot of weekly NPDES permit TN00002968 outfall 302 at Rogers Quarry (MBK 1.6) from March 1990 through April 1993. (a) NPDES reported total arsenic and arsenic speciation data. (b) NPDES NTU, flow, COD and pH.

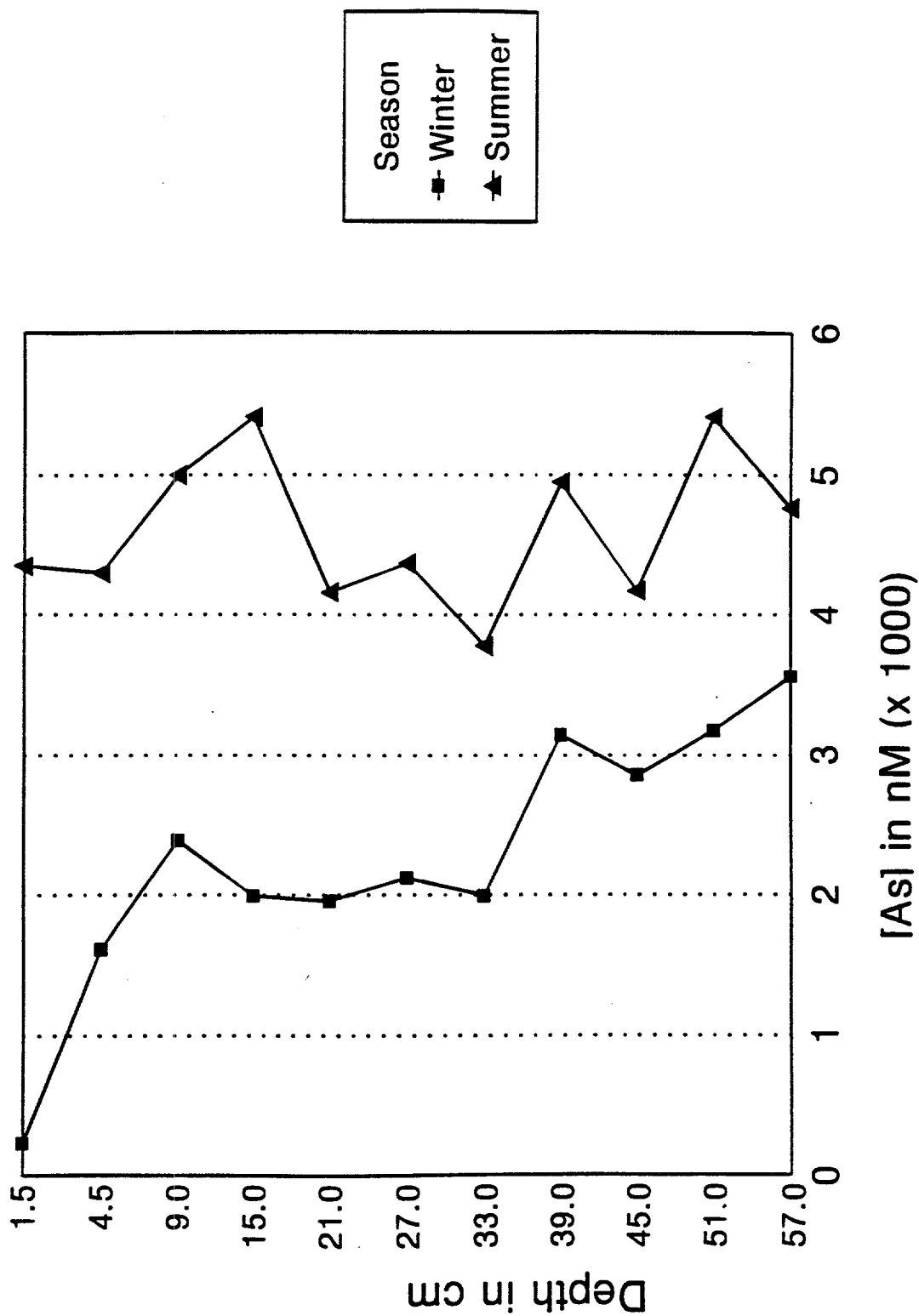


Fig. 14. Profile of total dissolved inorganic As (nM) in pore water by depth in the sediment for each season in upper McCoy Branch Embayment (MBK 0.7).

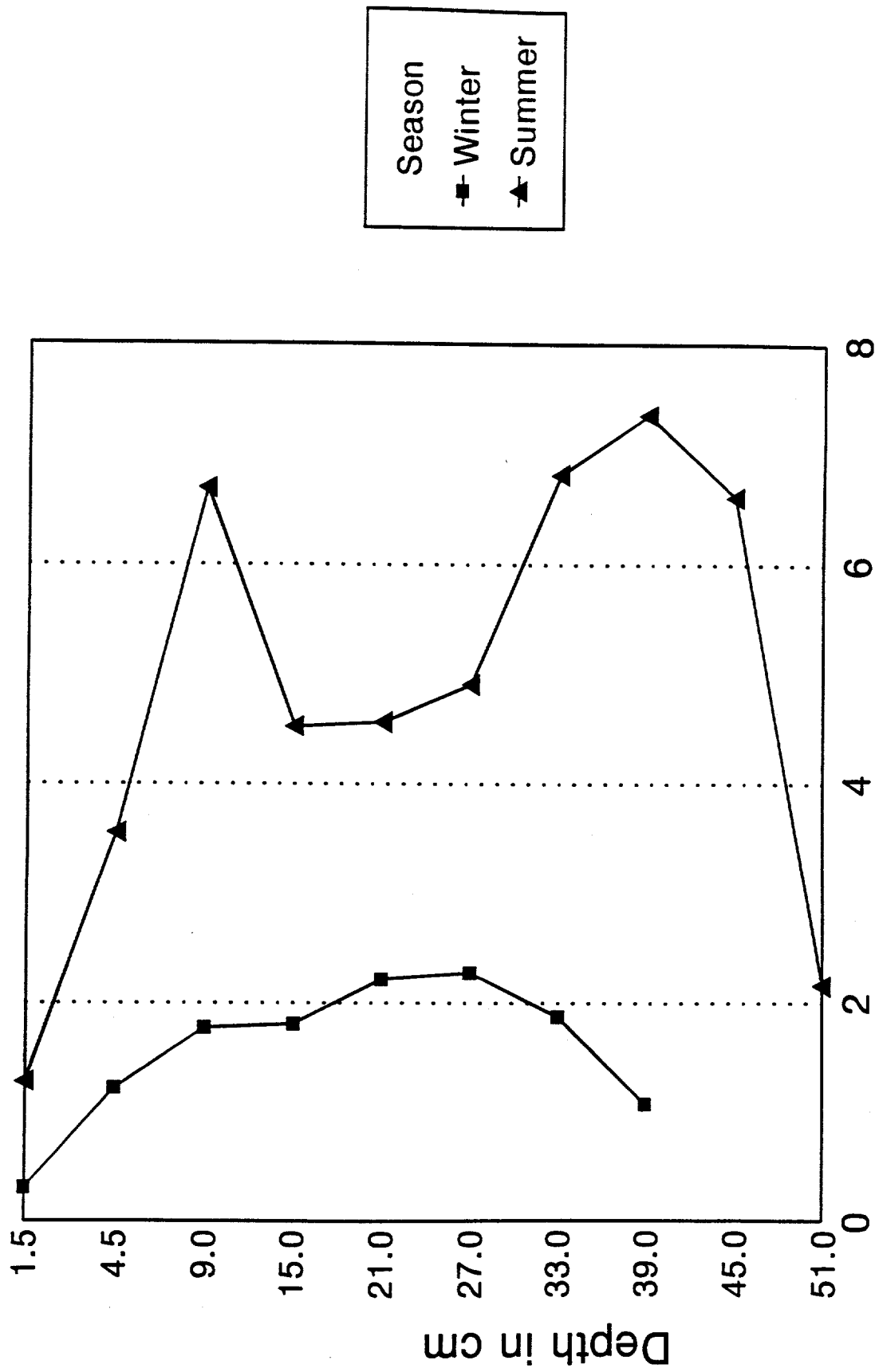


Fig. 15. Profile of total dissolved inorganic As (μM) in pore water by depth in the sediment for each season in upper McCoy Branch Embayment (MBK 0.85).

Table 31. Mean inorganic As, As(III), and As(V) concentrations (nM) for pore water in upper McCoy Branch for each season

Season	N	Inorganic As (Group)	As(III) (Group)	As(V) (Group)
Winter	19	1974 (B)	735 (B)	1239 (B)
Summer	21	4721 (A)	1937 (A)	2784 (A)

^aDifferent group letters (A, B) indicate significantly different F statistic values at a $p < 0.05$.

Table 32. Mean inorganic As, As(III), and As(V) concentrations (nM) for pore water by depth in the sediment of upper McCoy Branch^a

Depth (cm)	N	Inorganic As (Group)	As(III) (Group)	As(V) (Group)
1.5	4	1542 (BC)	604 (A)	938 (DC)
4.5	4	2670 (BCA)	1256 (A)	1413 (DCB)
9.0	4	3965 (BA)	1644 (A)	2320 (CBA)
15.0	4	3430 (BCA)	1631 (A)	1798 (DCBA)
21.0	4	3220 (BCA)	1496 (A)	1723 (DCBA)
27.0	4	3417 (BCA)	1454 (A)	1962 (DCBA)
33.0	4	3615 (BCA)	1502 (A)	2113 (DCBA)

^aDifferent group letters (A, B, C, D) indicate significantly different F statistic values at a $p < 0.05$.

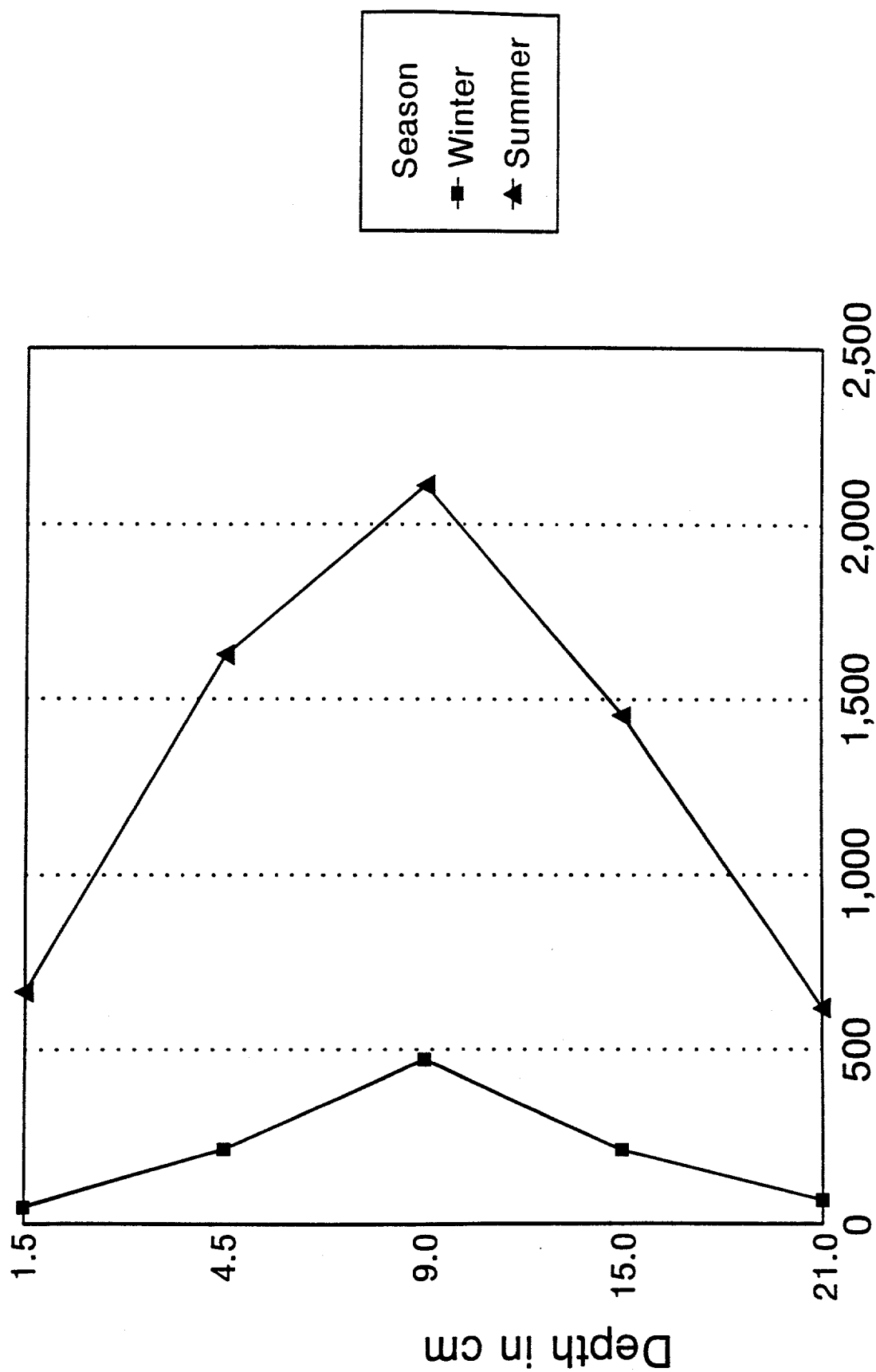


Fig. 16. Profile of total dissolved inorganic As (nM) in pore water by depth in the sediment for each season in lower McCoy Brancy Embayment (MBK 0.5).

Table 33. Mean arsenic, iron, and manganese K_D for each sediment depth in upper McCoy Branch^a

Depth (cm)	N	As K_D	N	Fe K_D	N	Mn K_D
1.5	4	1319 (A)	4	76,213 (A)	4	13,458 (A)
4.5	4	304 (B)	4	49,531 (AB)	4	753 (A)
9.0	4	204 (B)	4	23,935 (AB)	4	339 (A)
15.0	4	324 (B)	4	11,431 (B)	4	304 (A)
21.0	4	354 (B)	4	8,395 (B)	4	299 (A)
27.0	4	284 (B)	4	6,554 (B)	4	265 (A)
33.0	4	340 (B)	4	5,011 (B)	4	222 (A)

^aDifferent group letters (A, B) indicate significantly different F statistic values at a $p < 0.05$.

Table 34. Mean arsenic, iron, and manganese K_D for each sediment depth in upper McCoy Branch in winter and summer^a

Depth (cm)	Winter				Summer			
	N	As K_D	Fe K_D	Mn K_D	N	As K_D	Fe K_D	Mn K_D
1.5	2	2,334 (A)	110,070 (A)	26,300 (A)	2	304 (A)	42,356 (A)	616 (A)
4.5	2	458 (B)	64,000 (A)	1,320 (A)	2	146 (A)	35,061 (A)	187 (A)
9.0	2	284 (B)	34,250 (A)	444 (A)	2	125 (A)	13,620 (A)	234 (A)
15.0	2	434 (B)	13,096 (A)	294 (A)	2	212 (A)	9,767 (A)	314 (A)
21.0	2	498 (B)	9,329 (A)	325 (A)	2	209 (A)	7,462 (A)	274 (A)
27.0	2	377 (B)	6,348 (A)	278 (A)	2	191 (A)	6,761 (A)	253 (A)
33.0	2	381 (B)	4,690 (A)	217 (A)	2	300 (A)	5,332 (A)	227 (A)

^aDifferent group letters (A, B) indicate significantly different F statistic values at a $p < 0.05$.

Table 35. The mean inorganic As, AsIII, and AsV concentrations (nM) from each site during winter^a

Site	N	Mean Inorganic As (Group)	Mean AsIII (Group)	Mean AsV (Group)
TRK 849.6	18	2.89 (A)	0.05 (B)	2.84 (A)
TRK 863.2	8	3.11 (A)	0.10 (B)	3.01 (A)
TRK 907.2	6	2.48 (A)	0.09 (B)	2.39 (A)
CRK 1.6	10	7.1 (A)	0.05 (B)	7.26 (A)
CRK 4.0	1	6.75 (A)	0.07 (A)	6.68 (A)
CRK 5.6	1	4.41 (A)	0.04 (B)	4.37 (A)
CRK 8.0	5	2.71 (A)	0.03 (B)	2.68 (A)
PCK 1.6	9	1.78 (A)	0.22 (B)	1.56 (A)
CRK 60.5	6	3.41 (A)	0.03 (B)	3.38 (A)
MBK 0.3	23	4.94 (A)	0.25 (B)	4.69 (A)
MBK 0.5	5	8.36 (A)	0.11 (B)	8.25 (A)
MBK 0.7	6	27.09 (A)	0.66 (AB)	26.43 (A)
MBK 0.9	1	18.18 (A)	1.19 (A)	16.99 (A)
CRK 66.7	1	4.59 (A)	0.04 (B)	4.55 (A)
CRK 80.0	1	3.41 (A)	0.07 (B)	3.34 (A)

^aDifferent grouping letters (A, B) indicate significantly different F statistic values at a $p < 0.05$.

Table 36. The mean inorganic As, AsIII, and AsV concentrations (nM) from each source during winter, spring, and summer^a

Source	Winter				Spring				Summer			
	N	Mean Inorganic As (Group)	Mean AsIII (Group)	Mean AsV (Group)	N	Mean Inorganic As (Group)	Mean AsIII (Group)	Mean AsV (Group)	N	Mean Inorganic As (Group)	Mean AsIII (Group)	Mean AsV (Group)
Lower Watts Bar Reservoir	26	2.96 (B)	0.06 (B)	2.9 (B)	28	2.00 (B)	0.05 (C)	1.95 (B)	49	4.41 (DE)	0.36 (C)	4.05 (CD)
Kingston	23	4.89 (B)	0.06 (B)	4.83 (B)	24	2.27 (B)	0.06 (BC)	2.21 (B)	33	8.80 (B)	0.97 (B)	7.83 (B)
Poplar Creek	9	1.78 (B)	0.22 (B)	1.56 (B)	3	1.29 (B)	0.00 (C)	1.29 (B)	18	5.78 (CD)	0.31 (C)	5.47 (BC)
Lower McCoy Branch	34	5.18 (B)	0.19 (B)	4.99 (B)	17	4.70 (B)	0.25 (ABC)	4.45 (B)	41	8.04 (BC)	1.19 (B)	6.85 (B)
Upper McCoy Branch	7	25.82 (A)	0.73 (A)	25.09 (A)	3	55.5 (A)	0.51 (A)	54.99 (A)	9	65.38 (A)	6.57 (A)	58.81 (A)
Bull Run Steam Plant	2	4.00 (B)	0.06 (B)	3.94 (B)	3	2.7 (B)	0.36 (AB)	2.34 (B)	9	2.72 (E)	0.38 (C)	2.34 (D)

^aDifferent grouping letters (A, B, C, D, E) indicate significantly different F statistic values at a p<0.05.

Table 37. Mean inorganic As, As(III), and As(V) concentrations (nM)
for pore water from each source

Source	N	Inorganic As (Group)	As(III) (Group)	As(V) (Group)
Lower Watts Bar Reservoir	76	151 (C)	52 (B)	99 (C)
Kingston	61	365 (C)	109 (B)	256 (C)
Poplar Creek	71	38,889 (A)	31,313 (A)	7,575 (A)
Lower McCoy Branch	114	510 (C)	161 (B)	349 (BC)
Upper McCoy Branch	40	3,417 (B)	1,367 (B)	2,050 (B)

^aDifferent grouping letters (A, B, C) indicate significantly different F statistic values at a $p < 0.05$.

Table 38. Mean arsenic, iron, and manganese K_p in sediment and statistical significance grouping values for each sampling area, divided by source and site^a

Sampling area	N	As K_p	N	Fe K_p	N	Mn K_p
Source						
Lower Watts Bar Reservoir	62	862 (A,B)	45	22,921 (A)	46	339 (A)
Kingston	32	343 (B)	26	38,139 (A)	27	523 (A)
Poplar Creek	47	313 (B)	39	68,504 (A)	38	187 (A)
Lower McCoy Branch Embayment	83	1298 (A)	60	35,723 (A)	62	1042 (A)
Upper McCoy Branch Embayment	40	380 (B)	38	20,091 (A)	38	1699 (A)
Site						
TRK 849.6	62	862 (A,B)	45	22,921 (A)	46	339 (A)
CRK 1.6	32	343 (A,B)	26	38,139 (A)	27	523 (A)
PCK 1.6	47	313 (A,B)	39	68,504 (A)	38	187 (A)
CRK 60.5	16	1557 (A)	16	16,838 (A)	16	821 (A)
MBK 0.3	57	1355 (A)	40	44,583 (A)	42	1178 (A)
MBK 0.5	10	559 (A,B)	4	22,673 (A)	4	503 (A)
MBK 0.7	22	479 (A,B)	20	19,633 (A)	20	340 (A)
MBK 0.85	18	259 (B)	18	20,600 (A)	18	3210 (A)

^aDifferent group letters (A,B) indicate significantly different F statistic values for each grouping at a $p < 0.05$.

5. DISCUSSION

This chapter discusses surface water quality, arsenic speciation, and other data that contribute to the dynamics of arsenic in the CR/WBR system and compares observed values with risk screening criteria previously presented in Chap. 1. Discussion includes comparisons between sites, as appropriate, to provide a more complete spatial/temporal view of arsenic dynamics in the CR/WBR system. Results are also discussed in terms of the conceptual model for arsenic dynamics, as presented in Chap. 2 and in Fig. 1. A physical model of arsenic movement in the CR/WBR system will be proposed. For this study, all pore water and water column arsenic is dissolved. Also, 99% of the surface water total inorganic arsenic data presented is As(V) (Appendix A in Volume 2). Unless otherwise noted, total inorganic arsenic is presumed to be primarily in the oxidized state [As(V)].

Background concentrations of arsenic species in the CR/WBR system were measured for surface water sites upstream from the BRSP (CRK 78.3, CRK 80). These values are not significantly different from those measured downstream from the BRSP (CRK 73.6, CRK 66.7), immediately downstream from the McCoy Branch Embayment at CRK 60.5, those measured in Poplar Creek (PCK 1.6), or those measured in LWBR (TRK 849.6, TRK 863.2, TRK 875.2) (Table 39). Arsenic was not detected in either Norris Reservoir or Poplar Creek during the first phase of the Clinch River Remedial Investigation, though the detection limits were much higher (approximately 13 nM or 1 $\mu\text{g/L}$) (Appendix F, Table F.2, Cook et al. 1992) than those used in this study (approximately 0.04 nM or 0.003 $\mu\text{g/L}$). The values for surface waters at the sites listed above are well below the detection limits of standard analytical techniques and considered background for the purposes of this study.

LOWER WATTS BAR RESERVOIR

Water quality conditions observed during summer were within the normal range for moderately deep reservoir systems (Thornton et al. 1990). Increases in bottom water inorganic arsenic occurred to an observable degree during the summer in LWBR (TRK 849.6) at water column depths corresponding to low (but detectable) DO values (Fig. 3). The flux of arsenic from the sediments to the water column, based solely on observed water column, pore water, and sediment solids arsenic concentrations (not flux calculations) is likely the source of increased arsenic levels at TRK 849.6 (Figs. 4 and 5). Arsenic results for LWBR are consistent with the model of arsenic dynamics presented in Fig. 1. This should be considered as a natural phenomenon and not of concern to human health or ecological risk because of both the levels of arsenic (less than 10 nM) and the depth of the water column (25 m) at the LWBR site. Rudimentary arsenic flux calculations are proposed to confirm this observation.

KINGSTON

Elevated surface water temperature values in the top 0.5 to 3 m corresponded with the peak inorganic arsenic values in the Kingston area during spring, summer, and fall [Figs. 6 and 7(a-c)]. Arsenic concentrations were higher overall, and significantly higher during summer, at 0.5 m than they were deeper in the water column (Tables 2 and 6). However, water column DO values did not change with depth during summer, unlike those for LWBR and McCoy Branch Embayment. Surface water inorganic arsenic values were significantly greater at Kingston than in Poplar Creek or LWBR during summer [Table 14, Fig. 7(c)]. Taken as a whole, pore water arsenic values at CRK 1.6 were significantly higher in spring and summer

Table 39. The mean inorganic As, AsIII, and AsV concentrations (nM) from each site during spring and summer^a

Site	Spring				Summer			
	N	Mean Inorganic As (Group)	Mean AsIII (Group)	Mean AsV (Group)	N	Mean Inorganic As (Group)	Mean AsIII (Group)	Mean AsV (Group)
TRK 849.6	18	2.15 (B)	0.05 (B)	2.10	42	4.56 (D)	0.35 (CD)	4.21 (E)
TRK 863.2	5	1.63 (B)	0.06 (B)	1.57	7	3.52 (D)	0.43 (CD)	3.09 (E)
TRK 873.2	5	1.85 (B)	0.06 (B)	1.79	N/A	N/A	N/A	N/A
TRK 907.2	6	1.57 (B)	0.05 (B)	1.52	6	5.74 (D)	0.63 (CD)	5.11 (E)
CRK 1.6	10	2.98 (B)	0.06 (B)	2.92	20	8.57 (D)	1.05 (CD)	7.52 (DE)
CRK 4.0	1	4.06 (B)	0.16 (B)	3.90	1	23.0 (C)	1.40 (CD)	21.6 (C)
CRK 5.6	1	2.14 (B)	0.03 (B)	2.11	1	21.8 (C)	1.73 (C)	20.07 (C)
CRK 8.0	6	1.49 (B)	0.03 (B)	1.46	5	7.99 (D)	0.79 (CD)	7.20 (E)
CRK 18.4	N/A	N/A	N/A	N/A	1	5.38 (D)	0.09 (D)	5.29 (E)
PCK 0.25	N/A	N/A	N/A	N/A	1	5.80 (D)	0.14 (CD)	5.66 (E)
PCK 1.6	3	1.29 (B)	0 (B)	1.29	15	6.02 (D)	0.34 (CD)	5.68 (DE)
CRK 20.0	N/A	N/A	N/A	N/A	1	2.51 (D)	0.11 (D)	2.40 (E)
CRK 60.5	4	2.57 (B)	0.24 (AB)	2.33	11	2.43 (D)	0.21 (CD)	2.22 (E)
MBK 0.3	12	3.81 (B)	0.26 (AB)	3.55	25	8.59 (D)	1.17 (CD)	7.42 (DE)
MBK 0.5	1	24.0 (AB)	0.18 (B)	23.82	5	17.65 (C)	3.43 (B)	14.22 (DC)
MBK 0.7	1	31.7 (AB)	0.22 (AB)	31.48	6	52.47 (B)	6.87 (A)	45.60 (B)
MBK 0.9	2	67.4 (A)	0.65 (AB)	66.75	3	91.2 (A)	5.96 (A)	85.24 (A)
CRK 66.7	1	3.89 (AB)	0.75 (A)	3.14	6	2.79 (D)	0.42 (CD)	2.37 (E)
CRK 73.6	1	3.65 (AB)	0.31 (AB)	3.34	1	4.06 (D)	0.84 (CD)	3.22 (E)
CRK 78.0	N/A	N/A	N/A	N/A	1	2.0 (D)	0.01 (D)	19.9 (E)
CRK 80.0	1	0.62 (AB)	0.01 (B)	0.61	1	1.71 (D)	0 (D)	1.71 (E)

^aDifferent grouping letters indicate significantly different F statistic values at a p<0.05.

than in fall and winter (Table 9). Normal deposition of arsenic contaminated particles from sources near the Kingston and from natural erosion of coal-bearing rock higher in the watershed may be the source of arsenic in these sediments. Similar sources may be responsible for arsenic in sediments in LWBR. The values in these sediments are similar to those measured in LWBR and in Norris Reservoir for the first phase of the Clinch River Remedial Investigation (Appendix B in Volume 2, Table C.2 in Cook et al. 1992).

Comparing the surface water and sediments in the Kingston area with the conceptual site model for arsenic dynamics (Fig. 1) suggests that a source other than the local sediments or historic releases to Poplar Creek is responsible for elevated inorganic arsenic at Kingston. Further, inorganic arsenic values were significantly greater during summer for CRK 4 and CRK 5.6 than at other Kingston sites (TRK 907.2, CRK 1.6, CRK 8) (Table 10). This evidence suggests that the elevated levels of inorganic arsenic originated in the vicinity of the Kingston Steam Plant.

POPLAR CREEK

Review of water quality data for the Poplar Creek site indicates that there is no thermal or DO stratification during summer, conditions that are similar to those of a flowing system (Fig. 6, Appendix A in Volume 2). Surface water inorganic arsenic values were significantly higher deep in the water column (4 to 5 m) than they were in the shallow areas (0.5 to 4 m) during summer and fall [Table 11, Fig. 7(a-c)]. No significant differences with depth were observed during winter and spring. Arsenic levels during summer were significantly different from and less than observed in the Kingston area (Table 13).

Poplar Creek sediments were grossly contaminated with arsenic, with levels significantly different from, and at least an order of magnitude higher than, any other site (Appendix B in Volume 2, Table 18, Fig. 9). Pore water inorganic As and As(III) were significantly higher during winter than during spring or fall; summer inorganic arsenic was also significantly higher than spring and fall (Table 15). These patterns are very different from those observed at other sites (Tables 9, 24, and 40). Poplar Creek pore waters also differed from those of the other sites in terms of the proportion of As(V) to total inorganic arsenic present; the average percent value for all Poplar Creek pore waters was 19%, while all other sites ranged from 50 to 80% As(V) (Appendix B in Volume 2). Low As(V) proportions are consistent for all sediment depths below 4.5 cm; the surface sediments were in the same range as, and not significantly different from, other sites, including LWBR and Kingston (Appendix B in Volume 2, Table 19).

Table 40. Mean inorganic As, As(III), and As(V) concentrations (nM) for pore water in lower Watts Bar Reservoir

Season	N	Inorganic As (Group)	As(III) (Group)	As(V) (Group)
Winter	12	121 (A)	21 (B)	100 (A)
Spring	12	117 (A)	38 (AB)	79 (A)
Summer	42	178 (A)	65 (A)	113 (A)
Fall	10	114 (A)	55 (AB)	59 (A)

^aDifferent grouping letters (A, B) indicate significantly different F statistic values at a $p < 0.05$.

Analysis of K_D data yields a very different picture from pore water contaminant concentrations. Arsenic K_D values were only significantly different from those for CRK 60.5 sediments, while Fe and Mn were the same as all other sites (Table 38). Arsenic and Fe K_D s did not change significantly with season; spring Mn K_D values were significantly higher than for summer or fall (Table 16). Arsenic K_D values were significantly higher in surface sediments than at depth, reflecting the shift from reducing to oxidizing environments near the sediment/water interface (Table 17, Fig. 1).

Inorganic arsenic in Poplar Creek does not appear to conform to the simple conceptual model for arsenic dynamics (presented in Chap. 2), and it appears to behave differently at this site as compared with other sites. Low water column values, relatively low surface sediment values, and the dramatic increase in As(V) proportions in surface sediments suggest that the highly contaminated deep sediments are isolated from the surface water by a layer of cleaner sediments, deposited since fly ash sluicing operations were halted. An alternative suggestion is that there is a continuous flux of inorganic arsenic across the steep concentration gradient from the deeper sediments to the surface water, with water flow conditions in Poplar Creek diluting the arsenic and transporting it downstream. Performing flux calculations, based on concentration differences between depths in the sediment, for movement of arsenic from sediments to surface water may provide more definitive answers about the comparability of Poplar Creek with other sites and about whether contaminants are actually isolated from the surface waters or they are being diluted by the surface waters in Poplar Creek.

MELTON HILL RESERVOIR AND LOWER McCOY BRANCH EMBAYMENT

Trends in water quality in the LMBE area are similar to those for other areas studied, that is, they are undergoing seasonal thermal stratification with small changes in DO [Appendix A in Volume 2, Fig. 10(a-b)]. However, surface water quality in the BRSP area reflects that of a flowing river system, influenced by discharges from Norris Reservoir, which is 50 km upstream (Appendix A in Volume 2). Arsenic dynamics in both of these areas conform to the general conceptual model for arsenic dynamics in freshwater systems (Fig. 1). Surface water inorganic arsenic in LMBE was highest for all seasons and depths at MCBK 0.5 (14 nM), followed by MCBK 0.3 (6 nM) and CRK 60.5 (2.7 nM). Differences between sites were significant (Table 10). Surface water concentrations were significantly higher in winter than in other seasons at CRK 60.5, though no significant differences were observed with water column depth (Table 2). Surface water arsenic levels at MCBK 0.3 were highest in summer; no significant differences were observed with water column depth (Tables 2 and 6). Surface water inorganic arsenic values at MCBK 0.5 were not significantly different with season or with water column depth; however, summer As(III) levels were significantly higher than either winter or spring. Spring As(V) values were higher than winter (Tables 2 and 6). Arsenite [As(III)] values for 4 m deep in the water column, near the sediment/water interface, were significantly higher than for all other depths (Table 2).

Considering all LMBE sites, these patterns, which appear to be a function of the proximity of each site to the UMBE and RQ, held up for all seasons, though differences between CRK 60.5 and MCBK 0.3 were not significant in winter and spring (Tables 10 and 11). Winter and spring arsenic concentrations in LMBE were highest at the water surface for MCBK 0.5, declining with depth and distance downstream [Tables 2 and 10, Fig. 12(a-c)]. Summer values were significantly higher for bottom water (4 to 5 m) than for intermediate depths (2 to 3 m), though they were not significantly different from upper portions of the water column (0.5 to 1 m) [Table 12, Fig. 12(a-c)]. These observations suggest a decline in

arsenic concentrations with increasing distance downstream from UMBE and RQ (Table 10). Values for the BRSP fell in the range of what would be expected for uncontaminated sites (Appendix A in Volume 2).

Summer pore water arsenic values followed the same trends in LMBE as were observed for surface water, being significantly higher at MCBK 0.5 than at other sites (Table 22, Figs. 16, 17, and 18). Winter pore water values were significantly higher at MCBK 0.3 than at other sites (Table 25). Seasonal changes in surface water quality may have more of an impact on sediments at MCBK 0.5 than at the other sites, given that the average arsenic concentration declined by more than 1000 nM from summer to winter at MCBK 0.5, compared with 170 nM at MCBK 0.3 and 75 nM for CRK 60.5 (Appendix B in Volume 2). No patterns with season or sediment depth were discernable for As, Fe, or Mn K_D values (Appendix B in Volume 2). Flux of arsenic from the sediments at MCBK 0.5 and MCBK 0.3 flowing into LMBE during summer appears to be one source of elevated arsenic in LMBE surface waters, with UMBE serving as the other source. Seasonal changes in water quality reduce the release of arsenic from sediments to the surface water during winter and transport from upstream contributes to elevated levels.

UPPER McCOY BRANCH EMBAYMENT AND ROGERS QUARRY

Surface water conditions in UMBE reflected those of a shallow, seasonally stratified lake. Surface water was stratified with respect to both DO and temperature in summer; temperature and DO were uniform for all depths during winter. Though summer temperature values were only 2°C colder at depth, the apparent lack of water column mixing was evidenced by the 50% drop in DO values between 2 and 3 m deep [Fig. 10(a-b), Appendix A in Volume 2]. Arsenic levels in UMBE were significantly higher (20 to 50 nM inorganic arsenic) than all sites other than RQ for all seasons (Table 13). Average summer As(III) values were also significantly higher than for any other site, excluding RQ (Table 36). However, considering As(III) as a proportion of the total inorganic arsenic, As(III) accounted for 7% of total inorganic arsenic in UMBE, compared with 2% for the RQ outfall. At MCBK 0.7, summer inorganic arsenic values increased by an order of magnitude with depth in the water column, with a similar increase in As(III). These trends were exactly opposite to the thermal and DO stratification observed here [Figs. 10(b) and 12(c)]. A much less dramatic change in inorganic arsenic values with depth was observed for the MCBK 0.85 site, though there were no significant differences between these sites (Table 10). Average surface water arsenic values were two to four times lower in winter than during summer (Appendix A in Volume 2), changes that may be related to the elimination of stratified conditions associated with seasonal cooling of the surface water.

Surface water arsenic values were highest in the RQ effluent (Appendix A in Volume 2, Table 13). NPDES data for 1990 through 1993, collected weekly, showed seasonal trends in basic water quality parameters, with elevated COD in summer over other seasons. Comparing weekly NPDES water quality data with weekly arsenic speciation results suggests that there were no closely connected relationships between the parameters measured and arsenic concentration [Fig. 13(a,b)]. Visual inspection of the NPDES data suggests that water discharge and turbidity tended to vary in the same direction at the same time. COD and pH, which showed large seasonal shifts during the early years of this study, were relatively disconnected from seasonal processes after summer 1991. Sluicing of fly ash directly into RQ, reported previously (Turner et al. 1986; Ryon 1992), was curtailed during the course of this study, with a resulting improvement in water quality and a decrease in arsenic releases [Fig.

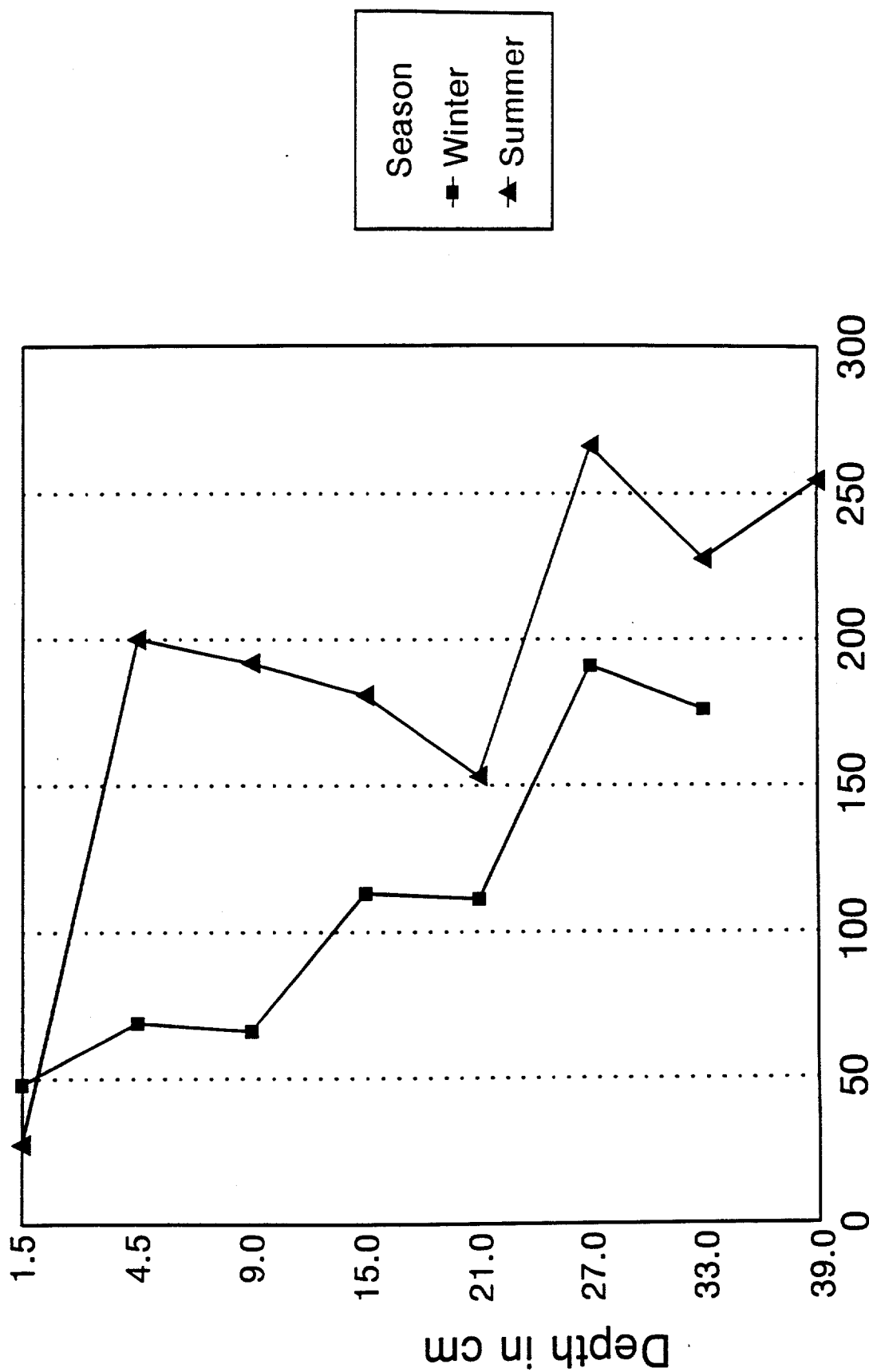


Fig. 17. Profile of total dissolved inorganic As (nM) in pore water by depth in the sediment for each season in Melton Hill Reservoir, downstream from lower McCoy Branch Embayment (CRK 60.5).

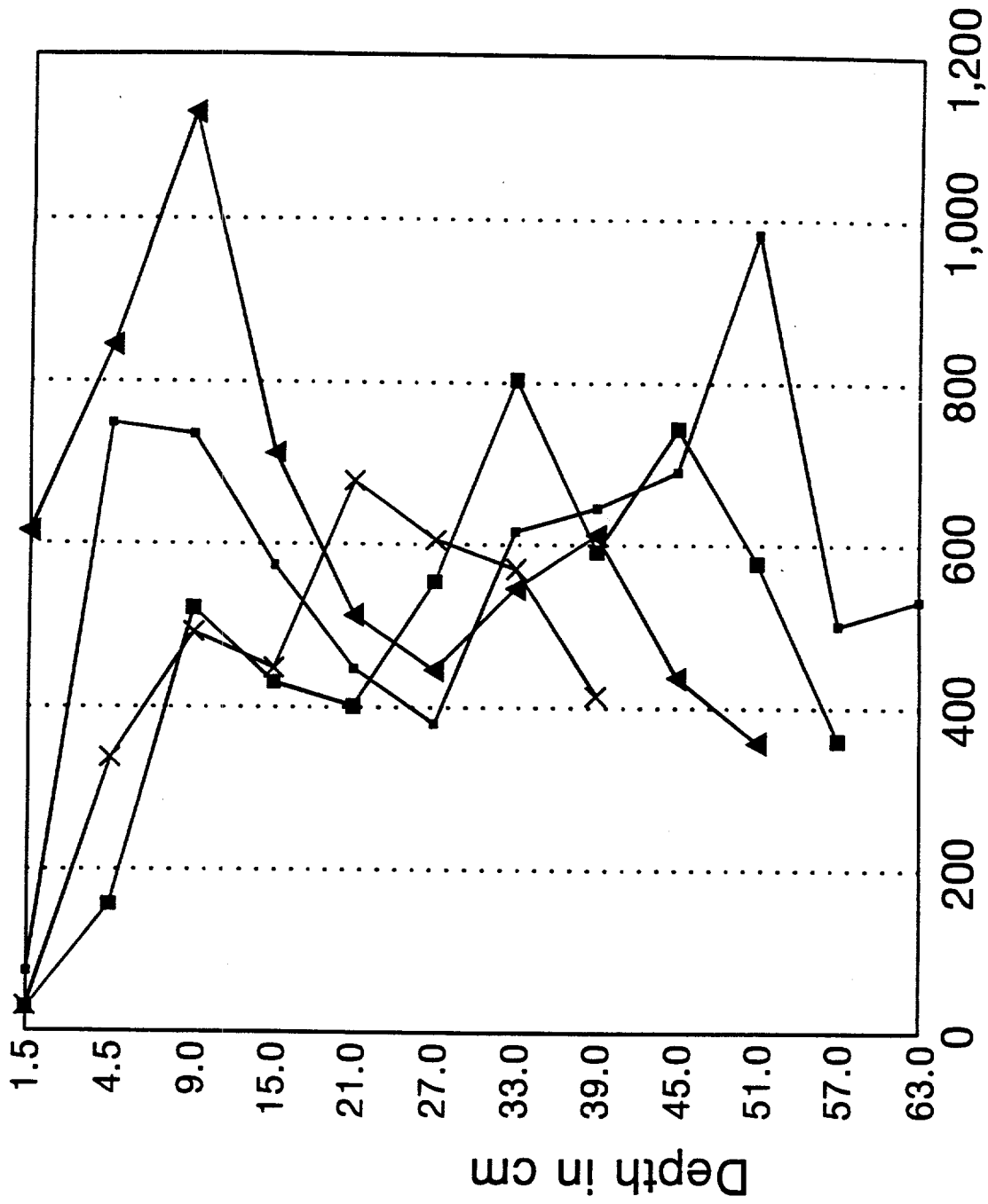


Fig. 18. Profile of total dissolved inorganic As (nM) in pore water by depth in the sediment for each season in lower McCoy Branch Embayment (MBK 03).

13(a,b)]. However, arsenic concentrations still exceeded human health and ecological risk values. The water discharge elevation was modified from surface water to several meters deep during the spring of 1992 to reduce the pH of RQ effluent; however, this modification had no apparent impact on the overall quality of water flowing out of RQ [Fig. 13(a,b)]. The lowering of the RQ discharge depth may increase the potential for greater arsenic releases, based on elevated inorganic arsenic values recorded at depth in RQ profile data (Appendix A in Volume 2).

Water column arsenic concentrations that exceeded risk screening values were observed at several locations within UMBE [Fig. 12(a-c)]. Arsenic values were greater than human health risk screening criteria both for all observations at the RQ outfall (MCBK 1.6) and for summer observations in UMBE (MCBK 0.7 and MCBK 0.85). The high values at 3 m deep that were observed in UMBE were in cooler waters with lower DO levels relative to those for RQ (Appendix A in Volume 2). Because the warmer water from RQ should stay at the surface in UMBE, these conditions suggest that the arsenic in UMBE currently originates from a local sediment source rather than from RQ. Additionally, while dissolved inorganic arsenic values in the RQ outfall did not change significantly from June 1992 to December 1992, surface water arsenic values in UMBE declined by a factor of two to four [Appendix A in Volume 2, Table 6, Figs. 12(a-c) and 13(a)].

Summer pore water arsenic values were 3 to 50 times greater in the UMBE surface sediments than for surface sediments at any other site (Appendix B in Volume 2, Table 19). The gradient of increasing pore water arsenic with depth, observed at all other sites, was not present at MCBK 0.7 (Fig. 14); values did decrease with depth at MCBK 0.85, but surface pore water arsenic was still greater than for all sites outside of UMBE (Appendix B in Volume 2, Tables 19 and 32, Fig. 14). The following comparisons, which focus on the surface sediments, give a picture of the relative behavior of dissolved arsenic at the sediment/water interface between sites. Pore water inorganic arsenic in UMBE was primarily As(V), though the proportion of As(III) was higher than for surface sediments at all other sites, indicating that pore water chemical conditions were strongly reducing near the sediment/water interface (Table 19). Directly comparing surface sediments (<5 cm deep) in Poplar Creek with those in UMBE, summer pore water arsenic values were significantly greater at 4.5 cm and 5 times greater at 1.5 cm for UMBE than for Poplar Creek (Appendix B in Volume 2, Table 21, Figs. 9, 14, and 16). The trend was reversed for winter (Table 21). Implications are that much more arsenic may be moving from the sediment pore waters into the water column in UMBE than for any other site, including Poplar Creek, despite the presence of 10 times greater quantities of arsenic at depth in Poplar Creek.

Considering K_D for As, Fe, and Mn over all sediment depths, As and Mn were significantly lower, and, therefore, proportionally had much higher dissolved constituents in UMBE during summer than all other sites (Table 38). Values were not significantly different with Poplar Creek (Table 38). For the upper 4.5 cm of surface sediments, UMBE pore water As and Mn K_D values were 5 to 6 times lower than for Poplar Creek, supporting the hypothesis that more arsenic is moving from the sediments into the water column in UMBE than at Poplar Creek or any other site (Appendix B in Volume 2). During winter, the UMBE K_D values are similar to those at other sites (Appendix B in Volume 2, Table 28).

Inorganic arsenic in UMBE appears to behave similarly to that for MCBK 0.5, MCBK 0.3, and TRK 849.6, which fits the conceptual model for arsenic dynamics (Fig. 1). Seasonal increases in surface sediment inorganic arsenic concentrations may precede the transport of

arsenic from the sediments to the surface water. In the case of UMBE, there appears to be no separation of the highly contaminated sediments from the water column, as is hypothesized for Poplar Creek. However, the flow rates and exchange of water between Melton Hill Reservoir and UMBE during summer are very low, perhaps allowing an accumulation of arsenic from the sediments to the surface water without the dilution that might occur in a flowing system. As was suggested for Poplar Creek, flux calculations for movement of arsenic from sediments to surface water may provide more definitive answers about its comparability with other sites and with the physical model for arsenic dynamics in McCoy Branch.

The seasonal relationship between surface sediments and surface water arsenic concentrations in UMBE suggests that pore water arsenic from UMBE sediments is a more important factor controlling surface water arsenic concentrations in UMBE than RQ outflows [Figs. 12(a-c), 14, and 15]. Changes in surface water arsenic values elsewhere in the McCoy Branch Embayment may also be attributed largely to seasonal mobilization from contaminated sediments in UMBE, rather than from direct flow out of RQ.

PHYSICAL MODEL FOR ARSENIC DYNAMICS IN MCCOY BRANCH

It is likely that the arsenic contamination in these sediments originated with the fly ash disposal in the filled disposal basin upstream from RQ and in RQ itself. McCoy Branch arsenic likely originated as part of the fly ash solids when they were originally deposited. The following is a physical model for that transport process in McCoy Branch. The depressed DO values observed at depth in RQ (Appendix A in Volume 2), in concert with elevated pH levels, may have and continue to facilitate the solubilization of inorganic arsenic from the sediment and into the water column, either in relationship to ferrous or manganous complexes, as observed by Sealer and Martin (1989), Aggett and Kriegman (1988), and Kuhn and Sigg (1993), or by reduction of As(V) to As(III). This dissolved arsenic, with a seasonal range from 92% As(V) in summer to 99% As(V) in winter, is transported to the RQ water column either by molecular diffusion or during seasonal water column mixing, as observed by Aggett and O'Brien (1985) and Aggett and Kriegman (1988). This arsenic is then released from RQ into UMBE. Once in UMBE, the dissolved arsenic in the water column is converted back to insoluble forms and deposited onto the sediments to remain until conditions for release are observed once again. The combination of flow rates in McCoy Branch between RQ and the upper MCBK and the slow rate of water exchange between UMBE and Melton Hill Reservoir may contribute to the accumulation of arsenic in the upper McCoy Branch Embayment sediments.

McCoy Branch data collected for this study do not definitively answer whether the upper embayment sediments are a more significant source of arsenic to the McCoy Branch surface waters than RQ. Although this report contains no calculations of the net flux of arsenic from possible sources to sinks, the data collected should contribute to such calculations. To determine the dynamics of arsenic in MCBK, the fluxes of arsenic from the sediments to the surface waters should be calculated using an equation such as Ficks First law (Berner 1980). This flux calculation should then be tied to a contaminant transport model for this system. In its simplest form, such a model for contaminant flux in the system would include RQ input, dilution of RQ input by UMBE, flux from RQ input to the upper McCoy Branch Embayment sediments, input from upper MCBK sediments to upper embayment surface waters, dilution of upper embayment surface waters, and net flux of arsenic out of the upper embayment into lower McCoy Branch Embayment on a seasonal basis.

COMPARISONS BETWEEN THE KINGSTON AND POPLAR CREEK SITES

The observed elevated arsenic levels in the Kingston area were greater than those observed on the same sampling dates for the closest source on the ORR in Poplar Creek, which is 20 km upstream [Table 13, Fig. 7(a-c)]. For the surface water arsenic observed in the Kingston vicinity to originate in Poplar Creek, the observed concentrations in the Poplar Creek water column would have to be approximately 12 times higher than that at Kingston to account for the dilution of the Clinch River (Table I.16 in Cook et al. 1993). During summer, when the peak arsenic concentrations were observed in the Kingston area [Fig. 7(c)], water temperatures in the Clinch River near Kingston normally are such that colder Clinch River water flows beneath warmer Watts Bar water (Fig. 6). This situation may begin as far upstream as CRK 10. Given this subsurface flow, any contributions from Poplar Creek to water quality or contamination in Watts Bar downstream from CRK 10 should be observable primarily in deeper waters. It may be concluded that the ash sluice pile at PCK 1.6 is not the source of elevated arsenic in the surface waters in the Kingston area.

COMPARISONS BETWEEN POPLAR CREEK AND McCOY BRANCH

Key differences between the ash disposed of historically in Poplar Creek and that in RQ may be a much lower organic matter content in the sediments, much higher flow rates, and the lack of even moderately depressed DO values in Poplar Creek as compared with McCoy Branch [Figs. 6, 7(a-c), 10(a & b) and 12(a-c)]. The key chemical factors in the mobilization of arsenic from sediment pore waters, previously listed, help to overcome the much higher pore water and sediment solids arsenic concentrations in Poplar Creek as compared with McCoy Branch. If the Poplar Creek water column at or near the sediment/water interface were to become anoxic for an extended period of time, it is plausible that arsenic could be remobilized from the sediments in concentrations comparable to those seen from RQ. The influence of organic matter on arsenic flux from Poplar Creek sediments has not been evaluated.

COMPARISONS BETWEEN KINGSTON AND McCOY BRANCH

Comparing the McCoy Branch Embayment surface water contamination with that observed in the Kingston area, the elevated surface water arsenic values at Kingston are much more extensive in area than at McCoy Branch, affecting at least 10 km of river surface water [Fig. 7(a-c)]. The impact of McCoy Branch contamination is largely limited to the upper embayment (approximately 1 km), where values fall below all risk screening criteria 0.5 km downstream. If a more extensive investigation were conducted in the Kingston area, it is likely that an arsenic source proportionally similar in magnitude to that observed in McCoy Branch (RQ) would also be found for the Kingston source.

6. CONCLUSIONS

1. The quality of arsenic speciation data was good, with the routine achievement of detection limits that were a factor of 100 below the minimum risk screening criteria. However, some samples for ICP metals analysis may not have been properly preserved, and the analytical holding times for a number of samples for determination of major ions were not met.
2. Arsenic concentrations not significantly different from background levels were observed for sites up and downstream of the BRSP (CRK 80, CRK 78.3, CRK 73.6, CRK 66.7), downstream of McCoy Branch Embayment (CRK 60.5), in the Poplar Creek area (CRK 20, PCK 1.6, PCK 0.25, CRK 18.4), and in LWBR (TRK 875.2, TRK 863.2, TRK 849.6).
3. Seasonal increases in dissolved inorganic arsenic in bottom waters at the Watts Bar Dam site were attributable to flux of dissolved arsenic from the sediments during low DO conditions.
4. Inorganic arsenic levels were greatest in surface waters (0 to 5 m deep) in the Kingston area. Values dropped with depth in the water column and were at their lowest near the sediment/water interface. An arsenic source to the surface water in the Kingston area is suspected. Surface water arsenic contamination in this area does not appear to originate on the DOE ORR.
5. Sediments in Poplar Creek are grossly contaminated with arsenic. However, no surface water contamination from the sediments in Poplar Creek greater than ecological risk values were observed. The Poplar Creek site (PCK 1.6) historically received fly ash directly from disposal operations at the K-25 Site on the ORR. These disposal operations were terminated in 1963. Surface water conditions and sediment chemistry may be preventing significant sedimentary release of arsenic to the surface waters in Poplar Creek.
6. Arsenic concentrations in RQ outfalls dropped greatly during this study as a result of actions taken to curtail and eventually eliminate fly ash disposal in RQ. However, arsenic concentrations in the RQ discharge were in excess of both human health and ecological risk screening criteria.
7. Seasonal increases in dissolved inorganic arsenic, a function of water column DO content, were observed both in the sediment pore waters and surface waters throughout the McCoy Branch embayment, downstream from RQ. Although increases were above some ecological risk screening criteria in upper McCoy Branch embayment, human health risk screening criteria were only exceeded in RQ and at the RQ outfall.
8. The conceptual model for arsenic dynamics, in which the seasonal mobilization to the water column from anoxic sediments is the primary source of arsenic, may be used to describe the dominant processes for arsenic flux in LWBR, LMBE, and UMBE. An alternative conceptual model is needed for Kingston and Poplar Creek.

9. Decreases in sediment pore water arsenic concentrations, not decreases in arsenic concentrations in the RQ outfall, contributed more to the decrease in inorganic arsenic in McCoy Branch surface waters. Changes in surface water arsenic values in McCoy Branch may be attributed largely to seasonal changes in sediment pore water chemistry, rather than changes in RQ outflows.
10. The apparent flux of arsenic from sediment pore waters to surface waters, based on observed concentration changes, was greatest in UMBE. Next highest were the Poplar Creek and Watts Bar Dam sites. No appreciable increases because of sediment release of arsenic were observed at Kingston.
11. The elevated surface water arsenic values at Kingston are much more extensive in area than at McCoy Branch. The impact of McCoy Branch contamination is largely limited to the embayment (approximately 1 km), where values fall below all risk screening criteria 0.5 km downstream. If a more extensive investigation were conducted in the Kingston area, it is likely that arsenic concentrations of a magnitude similar to those observed in RQ surface waters would be found at the Kingston contamination source.

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